Group Report

1964-36

E. W. Pike

Exploratory Preparation of Foils Strongly Colored in the 1 – 6µ Region of the Infrared

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LINCOLN LABORATORY

EXPLORATORY PREPARATION OF FOILS STRONGLY COLORED
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ABSTRACT

One aspect of a recent study was a search for a material approximating the following combination of qualities:

i.   A strongly "colored" reflectivity, specular or diffuse, in the near IR conforming closely to the schedule: $>5\mu$, 1.0 reflectivity; 4μ, 0.9; 3μ, 0.8; 2.5μ, 0.7; 2μ, 0.45; 1.5μ, 0.3; 1μ, 0.2; $<0.8\mu$, <0.1.

ii.   Minimum absorption at all wavelengths.

iii.   Minimum weight per unit area of reflecting surface, in the order of 1 gm/meter^2 (5000 sq. ft. /lb); this is the weight of a plastic foil about 1μ thick.

iv.   Easy dispersal, from storage in a compact form, into separated airborne flakes or bubbles, large enough ($>30\mu$ diameter) that diffraction effects will not distort the color, yet small enough to resist deformation by ordinary air turbulence.

v.   Cost, in the storage form, not exceeding $\$.02/\text{ft}^2$.

Three or more of these objectives, including always the first, can be met with any one of three different materials --- a surprising achievement in view of the completely unexplored state of the field in early 1962.

The Bound Brook Laboratories of the American Cyanamid Co., under subcontract from Lincoln Laboratory, found that pure smooth layers of copper 0.02μ (0.8 microinch) thick had very nearly the desired optical properties. Storage and dispersal of flakes of this thickness is obviously impractical, however; the bulk of the work was an effort to form or incorporate them into plastic microballoons formed by heating tiny suspended droplets of a foaming resin formulation. Chemical formation failed, but just before the project was cancelled (for unrelated reasons) they succeeded in showing that copper films of this thickness can be formed by evaporation in vacuum onto Mylar, dispersed by ultrasonic treatment into a foaming resin formulation, and spread evenly in the 1μ septa of a connected foam. Large-scale production of thin-walled microballoons from a foaming resin formulation was never attained.

This same laboratory showed that satisfactory films could be laid down on a substrate by evaporation in vacuum from titanium disulfide. The material, a previously undescribed titanium sub-sulfide, could probably be formed as free separate flakes by a gas phase reaction, but the very difficult control problems could not be attacked before the project was cancelled.

Finally, the Research Laboratory of the Corning Glass Company, also under subcontract from Lincoln Laboratory, succeeded in detaching free-standing flakes of fluorine-doped stannic oxide (previously known to be transparent in the visible but reflecting in the IR, when in the form of films on glass) from the substrate of soluble glass on which they had been formed. Again, optical and thickness objectives were met, but the dispersal requirement appeared intractible, and the cost was quite high.

A rather detailed account of both successful and unsuccessful trials is given here, as a contribution to the literature of an almost unexplored field.

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SPECIAL CERAMIC MATERIALS
(Corning Glass Company)

INTRODUCTION

As part of a longer study, Lincoln Laboratory undertook, early in 1962, to search for a film material combining extremely light weight and low cost with a strong and precisely stated "color" in the $1 - 5\mu$ region of the near infrared spectrum. Preliminary discussions quickly established that no similar requirements had been placed on any technology previously, so that this search became a program of exploratory research.

Subcontracts were negotiated with the Bound Brook Laboratories of the American Cyanamid Co. for exploration in the areas of dyes and plastics technology, and with the Research Laboratory of the Corning Glass Co. for a less extensive search in the fields of glass and ceramics technology. As the first explorations yielded one unexpected result after another, the stated objectives of these explorations were continually revised in response. Although this resulted in a larger ratio of "Brownian movement" to goalward progress than those concerned really hoped for, it led in the end to three different materials which met, to a greater or lesser degree, the established requirements.

Looking backward, it is fairly clear that there were five underlying objectives which did not really change during the optical and chemical research reported here, although they were not clearly recognized as such in the early stages of the work.

First the weight of the foil, per unit area of specularly or diffusely reflecting surface, had to be held close to 1 gram per square meter (5000 ft^2/lb), corresponding to a plastic film roughly 1μ thick.

Second, the spectral reflectivity of the film was required to diminish steadily with decreasing wavelength, forming a strongly "colored" material conforming reasonably to the following schedule of reflectivity as a function of wavelength: $>5\mu$, 1.0; 4μ, 0.9; 3μ, 0.8; 2.5μ, 0.7; 2μ, 0.45; 1.5μ, 0.3; 1μ, 0.2; $<0.8\mu$, <0.1. As the work progressed, inputs from other parts of the overall study forced the imposition, with constantly increasing strictness, of a requirement that absorption by the reflecting surface should be minimized at all wavelengths --- in other words, the surface should be transparent, rather than black, in the visible part of the spectrum.

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Another requirement, and in many cases the most difficult to meet, was that, starting from storage in some compact form, films of the desired properties should easily be dispersed or generated as separated airborne flakes or bubbles. These had to be large enough (>30μ in diameter) that diffraction effects did not distort the color, yet small enough that ordinary air turbulence would not crumple or otherwise degrade the extremely thin individual reflectors.

Finally, there were the ever-present elements of cost and safety. There was an upper bound on the cost at 2 cents/ft^2, under mass-production conditions. Many otherwise promising approaches were excluded by cost factors, or because they used poisonous or inflammable ingredients.

Since the whole general field was so unexplored, the Bound Brook Laboratories were requested, at the beginning of the exploration, to attempt a long leap forward. A preliminary survey had shown that pure smooth films of copper about 0.02μ thick had very promising properties, and the development of a foaming resin formulation which would not only form a microballoon of plastic when a tiny suspended droplet was heated, but which would also generate chemically a copper mirror of the proper thickness on one or both surfaces, was set as the objective. Resin formulations which reduced metallic copper from incorporated copper salts, during the process of curing, were not particularly difficult to develop, but the copper was always deposited in the form of very small, roughly spherical granules distributed through the body of the plastic. Once this was established as the general behavior, a thermodynamical argument was found which showed a very small probability for the formation of a copper mirror by chemical reduction of copper.

This understood failure led to a search for other methods for meeting the general objectives by a combination of copper and plastic. After several minor failures, it was found that suitable copper layers could be evaporated onto an acetone-soluble substrate in vacuum, freed from the substrate by dissolving the latter, and finally combined with a foaming resin formulation to form a copper-resin slurry. Foaming this slurry led to a connected plastic foam with flakes of copper spread flat in the thin septa;

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the reflectivity of the outer boundary of this foam had roughly the desired "color."

Mylar coated with about 0.02μ of aluminum was purchased from the National Metallizing Division of Standard Packaging Co., and it was shown that the aluminum could be removed from the backing, and dispersed in a resin formulation as a slurry of fine flakes, by a relatively simple ultrasonic operation. There seems to be no reason to doubt that copper could be similarly dispersed from Mylar coated in commercial production equipment. Counting both sides of each flake, the total cost of materials for a 1μ foil with 90% of its area reflecting would be in the order of $\$.05/meter^2$.

A similar leap into the technological unknown in the hope of a quick and inexpensive solution to the dispersal problem, by squirting a fine stream of a foaming resin formulation into a hot air stream to form first a mist of fine resin formulation droplets, and later an air-dispersed cloud of microballoons (a process first proposed by Raskin[1]), also failed. The pilot failures showed that the resin formulations used cured relatively slowly, so that attempts to produce a dense cloud of microballoons led to their sticking together into considerable clumps. It also showed that many of the bubbles apparently burst before attaining their calculated size, and that simple injection of a fine stream of liquid across a high-velocity air blast did not produce a sufficiently uniform atomization of the liquid. While it seems that successful manufacture of thin-walled microballoons from foaming resin formulations is probably within the state of the art of chemical engineering at present, there must obviously be a high degree of control over each step of the operation. Again, the study was terminated before the pilot failures could be followed up.

In the period after the initial failure to develop copper mirrors of plastic microballoons by reduction of copper salts, a large number of materials having a generally coppery or brassy appearance were tested for their infrared reflectivity spectrum. Among these substances was titanium disulfide, which combines a brassy color with a very flaky crystal habit, and which can be formed by a gas-phase reaction between titanium tetrachloride and hydrogen or ammonium sulfides. The disulfide itself had a

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poor IR spectral reflectivity, but a layer laid down on a glass substrate by evaporation in vacuum from a titanium disulfide mass proved to be excellent. The layer was apparently a sub-sulfide of titanium having an X-ray diffraction pattern different from any previously observed. With proper control, it might be able to produce flakes of this material by gas-phase reaction in a hot-air stream, but no experiments toward this end were authorized.

Finally, the Research Laboratories of the Corning Glass Co. had pointed out to me that properly "doped" coatings of stannic oxide on glass had been used for some time to reflect infrared energy while remaining transparent to visible light --- crane cab windows in steel mills being a typical application. By depositing a fluorine-doped stannic oxide film on a soluble glass backing, and later dissolving out the backing, they produced several square feet of free-standing stannic oxide film having a somewhat less steep variation in reflectivity than the objective set, and somewhat higher weight per unit area. This material has the great advantage of withstanding quite high temperatures (perhaps $600^\circ C$) without rapid deterioration. The manufacturing process is extremely costly, however, and no obvious means of reducing it to the order of $10/lb has been perceived.

Since the proposed operation which originally justified these explorations has been withdrawn for other reasons, these strongly colored IR reflectors have no immediate specific use. They do represent explorations into an area which is rapidly approaching the center of interest in connection with a number of types of problems. It seems worth while to present them in some detail, in the reasonable hope that some reader will find in them a solution to his problem.

With this in mind, the final reports from both the Bound Brook Laboratories of American Cyanamid Co. and the Research Laboratory of Corning Glass Co. are published below in full (with the exception of occasional sections concerned with contractual matters.)

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SPECIAL ORGANIC-BASE MATERIALS

Final Report

to

Lincoln Laboratory

from

Bound Brook Laboratories, American Cyanamid Company

Project Manager, Dr. W. B. Hardy
Investigators, Dr. Eugene Allen
             Dr. G. E. Gerhardt
             Mr. H. W. Whitten

Adapted for publication by E. W. Pike

I. INVESTIGATION OF MATERIALS HAVING REQUIRED PROPERTIES

A. Theoretical Consideration of Nature of Materials Required

1. Methods of Achieving High Reflectivity

We will consider briefly the two most common methods of achieving reflectivity and their relationship to the nature of the materials used. The first is reflectivity by multiple scattering from dielectric particles. Each individual particle reflects a small part of the light, absorbs some, and transmits the rest. The reflected and transmitted light strikes another particle, where the process is repeated. If the absorption coefficient of the material is low, and if the layer is sufficiently thick, most of the incident light is diffusely reflected from the surface. The two main requirements for good reflectivity in this case are high refractive index and low absorption coefficient.

The second common reflective process is that occurring from a metallic surface. In contrast to the first case, most of the light reflected on the first encounter, and the rest is absorbed (unless the metal is in the form of a thin film, in which case some small portion of the light may be transmitted). The fundamental requirement for high reflectivity in this case is electron mobility compatible with the frequency of the incident light. In the near-infrared, which is the region with which we are concerned in this investigation, the free electrons of most metals are able to move in phase with the radiant energy striking them, and therefore the reflectivity is high. However, in the ultraviolet, the frequency of the electromagnetic radiation becomes too high for the free electrons to be able to follow, and most metals do not behave differently from dielectric materials. Semiconductors having suitably placed plasma edges would also give good reflectivities in the near-infrared.

2. Optical Constants Required for High Specular Reflectivity

The specular reflectance for normal incident radiant energy is given for bulk material by the following equation:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \, ,$$

where n represents the real part and k the imaginary part of the complex refractive index of the material, $\underline{n}$, defined as $\underline{n} = n + ik$. The quantity k is the absorption index, and is related to the familiar absorption coefficient, α, of Lambert's Law ($I_x = I_o e^{-\alpha x}$) by the following equation:

$$\alpha = 4\pi k/\lambda ,$$

where λ is the wavelength of the radiant energy in vacuum. For nonabsorbing substances, $k = 0$.

We see from this equation that high specular reflectivity is associated with high values for k. If k is zero or very low, as it is for dielectrics, high specular reflectivity is associated with high values for n. (Note, however, that the R vs n curve has a minimum at $n = \sqrt{k^2 + 1}$, so that if two materials had the same high k value, the one with the higher n value would generally have the lower reflectivity.)

Metals, which are the best known materials having high specular reflectivities, owe this property to their high values of k.

Semiconductors, too, have high k values in many cases. It is much less common to find a material of high n and low k which would have a high enough specular reflectivity to function as a good reflector without the aid of multiple scattering. Even a refractive index of 2.9, which is roughly that of titanium dioxide, corresponds to a specular reflectance of only 0.24. However, it is entirely possible that compounds may be found with high enough real refractive indices to serve as efficient specular reflectors, even with very low absorption indices. Since a high real refractive index is related to high dielectric constant and polarizability, one would have to search for such a compound by considering elements in the lower right portion of the periodic table.

In summary, therefore, the materials which have the best chance of success in view of the requirements given are metals, semiconductors, and inorganic compounds of heavy elements.

B.   Study of Metallic Films

1.   Reasons for Using Thin Films

Because of the need for economizing weight, it is necessary that the reflector be in thin film, rather than bulk, form. An additional reason for using thin films, in the case of metals, is that most metals in bulk form have high uniform reflectivities through- out the near-infrared.

In order to obtain the desired reflectance curve, which rises from 1 to 6μ, we would expect that thin films would be needed, from the following considerations:

> Both the real and imaginary parts of the refractive index of metals generally increase with wavelength in the near-infrared region.
>
> Table I shows bulk optical constants for copper, silver and gold in the region 1 - 6μ:[1

TABLE I

BULK OPTICAL CONSTANTS OF METALS

	Wavelength, μ	n	k
1. Copper	0.87	0.35	3.85
	1.75	0.83	9.46
	2.25	1.03	11.7
	4.00	1.87	21.3
	5.50	3.16	28.4
2. Silver	1.00	0.24	6.96
	1.50	0.45	10.7
	2.25	0.77	15.4
	3.00	1.65	20.1
	4.50	4.49	33.3
3. Gold	1.00	0.24	6.7
	2.00	0.47	12.5
	3.00	0.80	19.6
	5.00	1.81	33.

If we substitute these values into the equation for bulk reflectivity at normal incidence given in the preceding section, we see that the reflectances at all wavelengths are very close to 1.0 because of the very large values of k. However, we also can see that in the case of each of these metals k increases markedly with wavelength. Accordingly, if we reduce the reflectivities by using thin enough films, we might expect that we would reach a point where the changes in k would make themselves felt.

To make these calculations, one must use equations derived from thin-film optical theory, as described in a subsequent section. Figure 11, solid line, shows a calculated reflectance curve of a free-standing copper film having a thickness of 55$\overset{\text{o}}{\text{A}}$, based on optical constants interpolated from those given in Table I. We see that this curve has the desired rising slope. It must be emphasized that the curve is probably incorrect, because the optical constants used apply to the bulk metal are not valid for thin films. However, the overall trend of increase in real refractive index and absorption index probably still is valid for thin films as well as bulk material. Optical constants suitable for thin-film calculation are hard to find.

2.   Preparation of Thin Films

Accordingly, it was decided to prepare thin films of several metals by vacuum evaporation and determine their specular reflectance curves in the near-infrared. The vacuum evaporator was a large bell jar equipped with a mechanical forepump and a diffusion pump capable of evacuating the system to 0.1μ of mercury. The metal, in wire form, was placed in a basket made of coiled tungsten wire having a diameter of 0.52 mm. through which a current of 25 amperes was passed to heat the wire. The films were formed on microscope slides held at a distance of 12 cm. from the tungsten basket.

The metals which were evaporated were copper, gold, nickel, aluminum, iron and tin. Films of varying thicknesses of each metal were made by varying the amount of metal in the basket.

3.   Specular Reflectivity of Metallic Films

Specular reflectance curves on all the evaporated films were run on a Perkin-Elmer Model 21 infrared recording spectrophotometer with specular reflectance attachment

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(angle of incidence 10°). An aluminum mirror was used as reference. Figures 1 - 6 inclusive present a selection of the reflectance curves obtained. Figure 1 shows reflectance curves of three copper films with different amounts of metal taken for the evaporation. Figures 2 and 3 show the same for gold and nickel. The curve obtained from the film prepared by evaporating 27. 2 mg. of copper has roughly the desired shape. The thickness of this film was about 250$\overset{\text{o}}{\text{A}}$ (as determined at Lincoln Laboratory).

The stability to aging of the desirable copper film in a laboratory atmosphere was determined by rerunning the reflectance curve of this film two months and three months after preparation. The curves, shown in Fig. 4, indicate that the film is adequately stable under these conditions.

To investigate the reproducibility of preparing a copper film by evaporation, three evaporations were carried out starting with 15 mg. of copper, three starting with 20 mg., and three additional evaporations starting with 27 mg. The curves shown in Figs. 5, 6, and 7, indicate an enormous variability in reflectance values. It appears that the copper film is very sensitive to parameters in the vacuum evaporation over which no control is possible with the particular equipment used. This may account for the great variation in optical constants for thin films reported in the literature. [2

On the basis of this work, it appears that copper is a suitable metal for further investigation. The problem of vacuum evaporation of metals was turned over to Dr. J. G. Mavroides of Lincoln Laboratory for further study.*

     C.   Study of Other Materials

          1.   Titanium Disulfide

Titanium disulfide (TiS_2) appeared to be an interesting substance for this work for several reasons. First, it is formed by a gas phase reaction at 500° - 600°C., and would therefore be ideal from an operational point of view, since it could be generated in free-standing form directly from pumpable liquids. Second, it grows in platelets with a brassy appearance, and has semiconducting properties.

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* Dr. Mavroides' carefully prepared films proved on measurement to have properties very similar to the stated objectives.

a. Preparation

Titanium disulfide was prepared by the method given in Inorganic Synthesis. [3

$$TiCl_4 + 2\ H_2S \longrightarrow TiS_2 + 4\ HCl$$
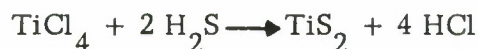
The method is to bubble hydrogen sulfide gas through titanium tetrachloride so as to saturate it with the latter, and then to pass the gas mixture through a tube heated to 500° - 600^oC.

The product collects on the wall of the tube and is scraped off after the reaction. If a smoke could be generated from titanium disulfide, it would have to be ejected from the generator as fast as it is formed.

b. Reflectivity Studies

An attempt to obtain a specular reflectance curve on a compressed pellet of titanium disulfide failed, as a smooth optical surface could not be prepared either directly from the die or by polishing.

A small portion of titanium disulfide was evaporated from a platinum boat onto a microscope slide in the vacuum evaporation unit. The temperature of the boat was not measured, but was judged visually to be well above $1,000^oC$. Reflectance curves of two films prepared in this way are given in Fig. 8. The curves, particularly the one at the bottom of the figure, have the desired combination of fairly high reflectivity and positive slope.

It was desired to see if the film on the slide was really titanium disulfide, or if decomposition had occurred during the evaporation. There was too little material for chemical analysis. X-ray diffraction patterns were run both on the film and on a sample of the starting material. Results are shown in Table II.

TABLE II

INTERPLANAR SPACING IN $\overset{o}{A}$ OBTAINED BY X-RAY DIFFRACTION ON TITANIUM DISULFIDE AND ON EVAPORATED FILM

Titanium Disulfide					Evaporated Film	
6.32		2.116	(s)		10.27	
5.71	(1)	2.053	(3)		10.12	
4.06	(s)	1.902			6.78	
3.93	(s)	1.705			6.52	
3.860	(s)	1.635			5.87	
3.559	(s)	1.631			5.43	
3.453	(s)	1.600			5.37	
3.348	(s)	1.599			4.54	
3.220	(s)	1.430			3.62	(3)
3.114	(s)	1.426			3.40	
2.855		1.311			3.259	(1)
2.626	(2)	1.270			2.819	(2)
					2.682	
					2.545	

(s) Orthorhombic sulfur line

(1), (2), (3) The three strongest lines

The diffraction lines of the film sample were quite weak, but still the results in Table II show without question that the film is not titanium disulfide. The spacings given could not be identified with any of the lower sulfides of titanium, the patterns of which have been published in the literature. [4, 5]

Incidentally, the pattern obtained from the titanium disulfide sample (Table II) was found to be identical with that published by Oftedal, [6] but improved in resolution. The data correspond to a hexagonal unit cell with parameters a=3.41Å, c=5.71Å, c/a=1.675.

The material remaining in the tungsten boat after the evaporation was also examined by x-ray diffraction. It produced a well-defined pattern which agreed neither with that of titanium disulfide nor with that of the film.

Attempts were made to prepare films of titanium disulfide by gently burnishing the material onto a substrate. Substrates tried were glass, cellulose acetate, polystyrene, polymethylmethacrylate, and polyethylene. Although the films had the typical brassy appearance of titanium disulfide, the infrared reflectivity was low.

The burnished film on polyethylene gave a specular reflectance curve from 3.5 to 10μ which was essentially constant at 10%. There was a slight peak in the neighborhood of $1.5 - 2\mu$.

Microscopical examination of the titanium disulfide starting material showed that the particles were considerably smaller than 1μ, which may explain the low reflectivity.

The titanium disulfide starting material, the burnished film on polyethylene, and the evaporated film were examined by x-ray fluorescence for sulfur to titanium ratio. The ratio of intensities of the sulfur line to the titanium line was found to be 0.50 for the starting material, 0.45 for the burnished film and 0.22 for the evaporated film. These figures do not represent absolute ratios of sulfur to titanium, but may be used between samples to compare sulfur content using titanium as a reference. The data clearly show that there is almost exactly half as much sulfur compared to titanium in the evaporated film as there is in the burnished film. (The higher sulfur ratio in the starting material is probably caused by the presence of a small amount of sulfur as impurity; this sulfur probably was not laid down in the burnished film.)

From the x-ray fluorescence data, we are led to believe that the evaporated film consists essentially of titanium monosulfide, or perhaps a mixture of lower sulfides which average to a ratio of one atom of sulfur to one atom of

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titanium. Since the evaporated film gave a satisfactory reflectance curve, it would seem to be important to identify this material further and determine if it possibly could be made by a gas-phase reaction.

In addition, a further attempt should be made to obtain a reflectance curve for titanium disulfide which would be truly representative of this material. A starting material of larger particle size may possibly produce a burnished film with higher reflectivity. Unfortunately, the arrival of the end of the contract period did not permit further work to be done on this phase of the project.

II. INVESTIGATION INTO METHODS OF INCORPORATING COPPER FILM INTO PLASTIC FOILS IN THE 1μ THICKNESS RANGE

Since thin copper films appeared to be suitable from the point of view of reflectance properties and stability, it was important to find a method of dispersal of the film. Finely divided free-standing film was considered impractical because of probable aggregation and "welding" during storage arising from the very high surface forces between adjacent film particles. Some sort of carrier is needed, and major consideration was given to foamed plastic microballoons. This aspect of the project is covered in detail in Mr. H. W. Whitten's section of the report. In the present work, we were concerned with methods of incorporating copper films into the plastic, and also with an alternative possibility of using a water-based system and floating colloidal copper particles to the surface of hollow aqueous spheres.

A. Theoretical Calculation of Effect of Substrate on Reflectivity

Since we are concerned with the use of plastic vehicle for the copper film, calculations were made of the effect of a plastic substrate on the reflectivity of the film. Three parallel series of calculations were carried out: the first for the case of the free-standing copper film, the second for the case of copper film backed by a layer of transparent plastic (the plastic film away from the light source), and the third for the case of copper film faced with a layer of transparent plastic (the plastic film toward the light source).

The equations used for the calculation are presented in Appendix II and a suitable Fortran program is given in Fig. II-1.

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The calculations were carried out with the optical constants for bulk copper. The values for the real and imaginary parts of the refractive index given in Table I were plotted against wavelength, and values for itermediate wavelengths were read off from the curves. The fact that these bulk optical constants did not apply to the films produced in the vacuum evaporator is strikingly illustrated by the fact that the calculated reflectance curve for a copper film having a thickness of 55Å shows fairly good agreement with the experimental reflectance curve found for a film having a thickness of 250Å. While it is undoubtedly true that the bulk metal optical constants are incorrect for films, a difference this great might possibly have been caused by contamination of the film. However, the calculations for the effect of the plastic substrate on reflectivity are probably still valid, even with the inappropriate optical constants for the metal. The substrate was assumed to have a refractive index of 1.5 throughout the calculations.

A much more serious restriction on the general validity of these calculations is that they were carried out for normal incidence only. In actual practice, the angle of incidence will vary with the relative positions of the sun, the cloud, and the observer. The effect of this restriction on the conclusions drawn from the calculations will be discussed below.

Figure 10 shows the effect of varying thickness of the plastic film on the reflectivity of the 55Å copper film at a wavelength of 4μ. The reflectance values show a sinusoidal variation with plastic film thickness. The effect is especially pronounced in the case of the metal film faced with plastic, the reflectance varying within limits of about 25% absolute. This is obviously an interference effect, and is mainly dependent on the ratio between the optical path length of the plastic film and the wavelength of the radiant energy.

We have been using a figure of 1μ as a reasonable thickness for the walls of the plastic microballoons. Since this thickness is of the same order of magnitude as the wavelengths of infrared radiant energy which we are considering, we would expect that this interference phenomenon would have a marked effect on the reflectance curve. As the wavelength in rising from 1μ to 6μ passes through certain values determined by the

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phase relationships between the singly and multiply reflected rays, we would expect reinforcement of the reflectivity. As it passed through certain other values we would expect interference with the reflectivity. These effects are shown in Figs. 11 and 12, which present calculated reflectance curves for the free-standing film and the combination metal and plastic films for two different thicknesses of plastic, 0.6μ and 1.0μ. The effects are pronounced, and the shape of the reflectance curve shows a considerable disturbance which is different for the two different thicknesses of plastic.

However, let us now imagine that we have a random film thickness, in which the plastic film may vary in thickness up to some maximum value. This would be the situation if the copper film is randomly incorporated into a much thicker plastic film so that the amount of plastic between the metal and the light source covers a range of values. The reflectance would now not be given by a single point on a graph such as that in Fig. 10, but would be calculated by

$$R = \frac{1}{d} \int_o^d R_x dx \, ,$$

where R is the averaged reflectance, R_x is the reflectance corresponding to a thickness x of the film, and d is the maximum value which x can attain. These values can be calculated by integrating curves such as those in Fig. 10 from zero thickness to the maximum thickness. We can easily see that this will effectively damp out the sinusoidal-type variations, except for very thin plastic films. The overall result will be a generally lowered reflectivity compared to that which would be achieved without the presence of the plastic film. This lowering of reflectivity values is appreciable; for example, in the case of 4μ radiant energy, as shown in Fig. 10, we see that the average lowering would be roughly 10% absolute, or 14% relative. The relative lowering of reflectivity would be even greater for lower reflectance values; we can estimate from Figs. 11 and 12 that in the present case we might expect a drop of close to 25-30% relative reflectance in the region of 2μ. Thus, the introduction of the assumption of random thickness does away

with the difficulty of playing havoc with the desired shape of the reflectance curve, but we are forced to conclude that the presence of the plastic film has a pronounced anti-reflective effect on the copper film. (This effect in fact helps to meet the requirement for a steeply falling reflectivity with decreasing wavelength. E.W.P.) As mentioned previously, these calculations must be considered only roughly quantitative, because of the various assumptions made. The use of the correct optical constants for copper in the film form would help, but probably the overall results are not affected too badly by the use of the bulk constants. More sophisticated calculations should assume that the system is 3-film rather than 2-film -- the metal film is really placed between two plastic films. Furthermore, provision should be made for the fact that the angle of incidence is not normal in the general case but can vary over a wide range. Among other things, a change in the angle of incidence would have the effect of increasing the path length through the film and therefore altering the phase relationships, so that in the case of the plastic film of constant thickness the various maxima and minima in the reflectance curve would occur at different wavelengths.

It is felt that when the more detailed calculations are carried out, however, the overall conclusions would be the same: in the first place it is necessary that the film thickness be allowed to vary randomly so as to avoid interference effects on the shape of the reflectance curve; secondly, the presence of the plastic film would have an overall anti-reflective effect amounting to some 10-30% relative in the region of 30-70% reflectivity.

        B.   In-Situ Formation of Copper Film

            1.   Mechanism of Film Formation

In considering the incorporation of copper film into a substrate, we have the choice of preparing the film in situ by chemical reduction of a copper compound or of directly incorporating copper film which has previously been prepared into the substrate. The first of these choices is obviously the more attractive, and therefore considerable effort was spent on trying to achieve this. Accordingly, it is pertinent to consider the mechanism of metallic film formation in order to decide whether it is feasible to produce such a film at the time the film is being generated.

The most commonly used methods of forming metallic mirrors can be grouped into two general categories, physical and chemical. The physical methods include vacuum evaporation, cathode sputtering and the like; the chemical methods involve reduction of a metallic salt in solution together with activation of the glass surface. Activation is usually effected by treating the glass with a solution of a metal salt such as stannous chloride; commonly used reducing agents are glucose and formaldehyde. [7]

In considering what these two widely divergent types of process might have in common, we see that there are certain requirements which must be met in order to produce a metallic film. First, there must be an overall free energy balance which is favorable. Secondly, there is a "rate of reaction" requirement which must be met. Considering the free energy balance first, we recognize that any surface contains a certain amount of surface energy, which represents the work required to produce that surface. This has the nature of a free energy, and may be designated for unit surface area by γ with units work/cm^2.

If the surface area of a material is changed, there is a free energy change represented by

$$\Delta F = \gamma \Delta \sigma,$$

where F represents free energy and σ surface area in cm^2.

Let us now consider the relative stability of copper in film form and in particulate form. In the process

$$Cu \ (particles) \longrightarrow Cu \ (free\text{-}standing \ film),$$

the free energy change is given by

$$\Delta F = (2\sigma_f - \sigma_p) \, \gamma_{Cu} \ ,$$

where σ_f represents the projected area of the film (the area of one side), σ_p the total surface area of the particles, and γ_{Cu} the surface energy per unit area of metallic copper (assumed to be the same for particles as for film). As a numerical example, if we assume that the film is 250Å in thickness, the particles have a diameter of 1μ, and the density of copper is 8.92 g/cm^3 both in film and in particulate form, then for 1 g of

copper $2\sigma_f = 8.97 \times 10^4$ cm^2 and $\sigma_p = 0.67 \times 10^4$ cm^2. Therefore $\Delta F = 8.30 \times 10^4 \gamma$. Although the value of γ is not known because surface energies of solids (in contrast to Liquids) are extremely difficult to determine, we can still see that the production of copper film from particles (of the dimensions given) would be accompanied by a large gain in free energy. Therefore, the film must be considered thermodynamically unstable compared to particulate copper.

Accordingly, in order to induce the metal to form a film rather than produce particles, we must somehow provide a means of dissipating the difference in free energy between the two states; in fact, if we could arrange for a concurrent reaction for which the decrease in free energy would be greater than the increase in free energy produced in going from particles to film, formation of film would be thermodynamically favored over formation of particles. Such a concurrent reaction is the attraction of the film to the substrate. In the reaction Cu (film, free-standing) + substrate $\longrightarrow$ Cu film on substrate, there is a loss of free energy caused by the attractive forces between the metal and substrate surfaces - the so-called free energy of adhesion. In fact, the attractive forces are largely caused by the fact that surface area and therefore surface energy are being destroyed. According to the equation of Dupre, the process of adhesion of one surface to another is accompanied by a free energy change which is given by

$$\Delta F = \sigma(\gamma_{AB} - \gamma_A - \gamma_B),$$

where γ_{AB} represents the interfacial energy between the two surfaces, and γ_A and γ_B represent the surface energies of the individual surfaces, all per unit area.

Now let us suppose that the substrate is metallic copper, as it would be after the first infinitesimal layer of copper film is laid down on any substrate. In this case, $\gamma_{AB} = 0$, $\gamma_A = \gamma_B = \gamma_{Cu}$, and the free energy change in going from free-standing copper film to deposited copper film is $\Delta F = -2\sigma_f \gamma_{Cu}$. We see that this loss of free energy exactly counterbalances the gain in free energy caused by forming the free-standing film. The overall free energy change in the process

Cu (particles $\longrightarrow$ Cu (film on substrate)

is therefore $\Delta F = -\sigma_p \gamma_{Cu}$, a loss caused by destroying the surface energy of the particles. Thus, once a copper film has started to form, additional copper will be called upon to add to this film rather than to form particles; in fact, in adding to the film, no new surface will be formed at all.

At the very start of film formation, however, an interfacial energy between the copper film and the substrate is created. This must necessarily be very low in all cases where films are produced, or else particles would be formed instead.

Summarizing the discussion on thermodynamic relationships, we can say that we cannot expect film formation without a surface on which the film will be laid down. Metal film in free-standing form can never be produced by reductive processes in solution. If films form at all, they form on whatever surfaces are available, in order that the free energy of adhesion may be utilized.

Turning now to the second requirement for film formation, we see that even though the thermodynamic requirements have been met there is a time factor which is very important. Based on our previous discussion, a suspension of copper powder in a copper beaker is a thermodynamically unstable system, but such a suspension may be kept for quite a long time before the copper will plate out on the beaker. In much the same way, a solution of silver salt and reducing agent used in silvering glass to produce mirrors is thermodynamically unstable, but still can be prepared before use without any reduction occurring. Only when contact is made with the glass (pretreated with a metallic salt solution) does reduction occur, and a mirror is produced. The best explanation for the catalytic effect of this pretreatment [8, 9, 10] appears to be that metal ions are absorbed from the pretreating solution onto the surface by a base exchange reaction. The reducing agent accumulates at the glass surface by preferential absorption (aldehydes, which are the usual reducing agents for this reaction, have capillary active properties). This leads to the formation of an extremely thin metal film; once this has been accomplished, the metal assumes the potential of the reducing agent and serves as the site for further metal deposition.

The time factor assumes great importance in our problem because of the extremely short time available to form a film. We showed thermodynamically that films can only form on surfaces. But before a film can possibly be formed, the copper, in whatever state it may exist, must first reach the surface. Thus, diffusional rates play a large part in the rate of film formation. In the case of metallic mirror formation from solution just considered, the rate of formation of the mirror, once it has started to form, is dependent on the rate of collision of metal ions and reducing agent molecules with the surface, and therefore on the rate of diffusion of these substances in solution. Probably the surface activity of the reducing agent provides a potential within the solution helping to bring the reducing agent to the surface, even after the mirror formation has been started.

Accordingly, if we are to be successful in forming copper films in situ at the time of formation of the plastic foil, we must first provide a surface capable of accommodating the film, and second, we must see to it that the film is formed in a short enough time. It would appear that we have no difficulty in providing enough surface since if we are making a foil we are automatically preparing surface in huge quantity. However, we are immediately faced with the problem of finding some way for the copper compound, dissolved or uniformly dispersed in the matrix, to reach the surface in the allotted time. If we are working with a plastic, we would expect the diffusional velocities to be very low. Even if we manufacture plastic films only 1μ thick and provide the most potent surface attractive forces for the molecules of the copper compound, film formation could not possibly occur in the time allotted for the formation of the plastic microballoons.

It therefore appeared that methods involving chemical reduction in solution would not be feasible. However, it seemed that there was some hope for methods involving thermal decomposition of copper compounds. In such a method, a copper compound is thermally decomposed to metallic copper with the evolution of a large quantity of gas. If particles of such a compound were incorporated in a plastic material and heated, each particle in decomposing would generate atomic copper and simultaneously surround itself with an envelope of gas. Accordingly all the copper atoms would be surrounded by a

plastic surface, and there is a possibility, however, far-fetched, that the copper vapor would condense on the plastic surface to form a film. As a method of film formation this idea is not new: Marboe and Weyl[8 report the formation of copper films by vaporizing copper compounds in a vacuum furnace and inserting a heated glass finger into the vapor. The glass finger was heated to a temperature high enough to decompose the vapor, and the copper mirror was produced directly on the finger. The situation in the plastic would be less favorable; the entire plastic would have to be heated to a high enough temperature to effect simultaneous vaporization and decomposition, and then one would have to hope that the presence of the gaseous decomposition products would not interfere with the formation of the film.

As a result of a literature survey, it was decided that the best chance of success would be to try the thermal decomposition of cupric formate.

2.   Thermal Decomposition of Cupric Formate

a.   Mechanism

The thermal decomposition of cupric formate has been studied by many investigators.[8, 11-18 In most cases, a copper mirror was observed as a by-product of the decomposition.

The most plausible mechanism for the decomposition appears to have been advanced by Keller and Korosy.[12 By a careful analysis of the decomposition products, these authors conclude that about 80% of the compound decomposes directly to copper, formic acid and carbon dioxide by the reaction

$$Cu\,(HCOO)_2 \longrightarrow Cu + HCOOH + CO_2 .$$
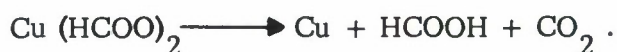
An additional 15% of the compound decomposes to cuprous formate by the reaction

$$2Cu\,(HCOO)_2 \longrightarrow 2CuHCOO + HCOOH + CO_2,$$

which then decomposes as follows:

$$2CuHCOO \longrightarrow 2Cu + H_2 + 2CO_2 .$$

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The cuprous formate takes the form of a finely
divided aerosol, and it is this material which is
held to be responsible for the formation of the
copper mirror. Accordingly, it would seem that
most of the cupric formate does not form a mirror
but goes directly to granular copper; only the cuprous
formate "vapor" will form the mirror, presumably
when it contacts another hot surface. However, this
mechanism is by no means clear cut.

Other investigators claim not to observe the volatile
decomposition product; the decomposition products
are often taken to be simply carbon dioxide and
hydrogen.

In view of the large quantity of gas liberated during
the decomposition of cupric formate, the idea was
entertained of using it as the blowing agent for the
microballoons as well as the film former. However,
the quantity of gas is too large by more than an order
of magnitude. It was decided, accordingly, to see first
if the film formation would occur, and to consider the
mechanics of bubble formation later.

b.   Decomposition Experiments in Plastic

Cupric formate was prepared by dissolving cupric
carbonate in dilute formic acid and allowing the
solution to crystallize. The crystals were filtered
off and dried at 60 - 70°C.

In preliminary experiments, cupric formate was incor-
porated into various polymers, and the plastic mass in
each case was placed in a chamber which was evacuated
to about 50μ of mercury and then filled with helium. The
chamber was heated to the decomposition temperature of
cupric formate, about 200°C, until the blue cupric ion
color disappeared.

In some of the preliminary experiments, an attempt was
made to dissolve the cupric formate in a solvent which
would be compatible with the polymer. In one case,
cupric formate was dissolved in trichloroethylene and
then incorporated into polymethylemethacrylate. In
another, cupric formate was dissolved in pyridine and
then incorporated into polystyrene. In still another
experiment, cupric formate was dissolved in water and
a polyvinyl alcohol film was prepared by adding the

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polyvinyl alcohol to the aqueous solution and allowing the mixture to dry. In each case, the polymer mixture containing both the cupric formate and solvent was allowed to air dry, and was then heated at about 50°C in a vacuum oven to remove all the solvent before preceeding with the decomposition.

Thermal decomposition of the cupric formate in the resulting polymer mixtures yielded no indication of film formation; small copper particles were always obtained. The polyvinyl alcohol film produced a shiny deposit which, however, turned out to have a very low specular reflectivity. The formation of the deposit may have been caused by the very large concentration of cupric formate in this particular film (about 30%).

Some experiments were conducted with polyurethane foams containing cupric formate. In one case, the cupric formate in powder form was placed with the polyester component of the formulation, the isocyanate component was added, and a foam was produced. Freon was used as the blowing agent. In the other case, the cupric formate was dissolved in water which was then mixed with the polyester and subsequently with the isocyanate to produce the foam; the water acted as the blowing agent. Here, too, the copper did not form a film but produced finely-divided particles.

Several experiments were now conducted with cupric formate in polystyrene. It was calculated that if we wish a ratio of 250Å of copper film to 1μ of polystyrene film, the ratio of copper formate to polystyrene should be roughly 1:2 if all the copper formate is assumed to produce the copper film. A mixture of 0.54 g. of cupric formate and 1.08 g. of polystyrene was dissolved in 25 ml. of toluene, and the solution was allowed to evaporate a little at a time from the same area of a glass plate. This produced a thick sheet about 10 cm in diameter. Portions of this film were heated at 200-225°C both in vacuo and in a helium atmosphere. The samples were cooled, cross-sectioned, and examined microscopically. No evidence of film formation was seen; tiny particles of copper were

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scattered throughout the field of view. The particles varied in size, but were about 10μ in diameter.

Another experiment was carried out by milling cupric formate in powder form into polystyrene, with a much smaller ratio of cupric formate to polystyrene this time. A 0.2 g. portion of the copper compound was placed on a three-roll mill with 100 g. of polystyrene, and thoroughly incorporated at 350°F. No decomposition of the cupric formate seemed to occur on the mill, and the mixture remained light blue.

Portions of this mixture were heated to 200°-225°C under various conditions - in vacuo, in an inert gas atmosphere, and in air. After the heating period, the plastic mass in each case was filled with small gas bubbles. It could not be determined by examination under the binocular microscope whether the plastic surfaces surrounding the bubbles were coated with copper film. Portions of the heated samples were then pressed out into films 10 mils thick by the use of a hydraulic press heated to about 300°F. Microscopical examination of these plastic films showed no evidence of the presence of broken copper film, but did show the usual well-dispersed copper particles.

However, another portion of the milled cupric formate-polystyrene mixture was ground with dry ice in a micro-mill so as to pass a 40-mesh screen. It was then heated in vacuo at 200°-225°C and later pressed into a 10-mil film. This film did contain broken strips and films of copper, in addition to the fine particles.

These experiments indicate that evolution of copper vapor within a gas bubble does not lead to film formation. But if the material is ground up before it is heated, and if the heating is done in vacuo, the gaseous decomposition products have an opportunity to escape. The copper vapor can then condense on the adjacent surfaces of the polystyrene particles, and film formation may occur. Of course these conditions cannot be realized in actual use.

c. Reflectivity of Film Containing Particulate Copper

It was desired to determine what the reflectivity of a plastic film which contained particulate copper, instead of copper film form, would be. The 10-mil films formed as described above were calculated to contain

about the same amount of copper per unit area
(2.23×10^{-5} g/cm^2) as would be present in a
metallic copper film $250\overset{\circ}{A}$ thick. Diffuse infrared
reflectivity measurements were made on the 10-mil
films in a hohlraum-type instrument at Grumman
Aircraft Engineering Corporation by Mr. R. J. Hemback.
A blank 10-mil polystyrene film was also run for
comparison. In no case and at no wavelength did
the film which contained the copper particles show
more than a 5% increase in reflectance over the blank
film. Thus particulate copper has little or no reflect-
ive properties compared to copper in film form.

d.   Attempts to Prepare Cuprous Formate

Since in the literature cited previously it was postu-
lated that cuprous formate is the active film-forming
material, some effort was devoted to the preparation
of this compound, in the hope that using it instead of
the cupric formate might give better results. The
only mention of cuprous formate preparation in the
literature is by Angel.[19] He used the reactions

$$Cu_2O + NH_4HCOO + NH_4OH \longrightarrow NH_4 \text{ complex of CuHCOO} \xrightarrow{HCOOH} Cu\,HCOO.$$
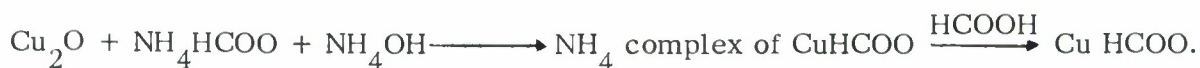
Angel pointed out that the preparation of this compound
is very difficult and it is very unstable, disproportiona-
ting to copper metal and cupric formate.
Attempts to use Angel's procedure were unsuccessful.
The following methods were also tried:

$$CuCN + HCOOH \longrightarrow CuHCOO + HCN\uparrow$$

No reaction occurred on standing at room temperature
over the weekend.

$$Cu_2O + 2HCOOH \xrightarrow{solvent} 2\,CuHCOO + H_2O$$

Anhydrous solvents such as benzene, ethanol, acetoni-
trile and ethyl formate were used. All these attempts
were unsatisfactory.

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$$CuCl_2 + 2NaHCOO \xrightarrow{CH_3CN} \left[Cu(HCOO)_2 \right] \xrightarrow{\text{powdered Cu}} CuHCOO$$

$$Cu(HCOO)_2 + \text{powdered Cu} \xrightarrow{CH_3CN} CuHCOO$$
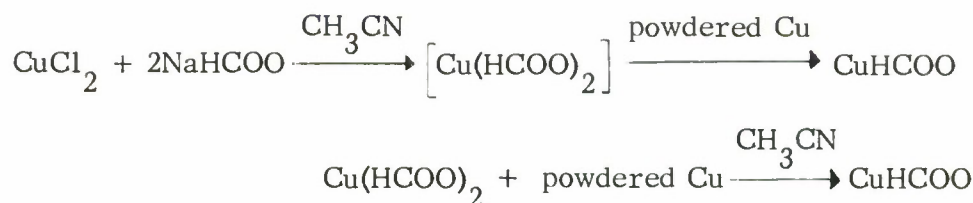
Both these reactions were also unsatisfactory. Summarizing the work on the thermal decomposition of cupric formate, we can say that it was completely unsuccessful. Since the possibility of producing films in this way was slim to start with in view of the arguments previously advanced, no further work along these lines is recommended.

3.   Flotation of Colloidal Copper

An entirely different sort of attack on the problem of forming copper film in plastic bubbles was based on the use of colloidal copper in an aqueous, rather than a plastic, vehicle. It is well known in the mining industry that it is possible to use flotation techniques to cause copper particles to be attracted to the interface between water and air. Under ideal conditions the individual particles would completely cover the interfacial area in a layer one particle thick. If the diameter of the particles were 250$\overset{o}{A}$, we would have an approximation to a uniform film of this thickness.

In ore flotation, an agent known as a "collector" is used. The collector ions are absorbed on the surface of the ore in such a way as to make the ore particles hydrophobic (or aerophilic). Subsequent aeration with a rapid current of air in the form of small bubbles causes the ore to be lifted to the top of the vessel, whence it is removed. In most cases a "frother" is also used, the function of which is to increase the interfacial area by the formation of a foam which is skimmed off. However, in a variant of the process known as skin flotation, no frother is used, and the ore merely forms a skin on the surface of the vessel.

In the application of this idea to our problem, the water would take the place of the plastic which we originally planned to use. Copper would be reduced in solution to give very small particles. The aqueous medium would contain a collector which would render the copper particles aerophilic. The slurry of reduced copper particles would then be

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injected into the atomization chamber, where it would be broken up into tiny droplets by the propellant gas. On being ejected out into a region of reduced pressure, the dissolved gases would be liberated, causing the droplets to become hollow (or, possibly, producing thin water films not necessarily in spherical shape). The viscosity would have to be high enough to prevent reformation of solid spheres at this point. The copper particles would arrange themselves at the surface, the water would freeze, and the result would be copper-coated ice particles.

Since the ice would eventually sublime, a water-soluble film former would have to be included. This substance could probably also be used to raise the viscosity, in order to prevent premature collapse of the films as noted above.

It was decided to conduct initial experiments with a gold sol instead of a copper sol. There was some question as to whether the individual particles of metal, even if floated as a mono-particle film, would be in good enough contact to form a conductive surface of sufficiently large dimension compared to the wavelengths of infrared radiant energy to give adequate reflective properties. If a floated gold film had a metallic luster, it could be concluded that the infrared reflectivity of such a film is good; if not, that it is not good. However, it was felt that copper, being prone to oxidation, would not given an unequivocal answer by simple visual inspection. Accordingly, the first experiments on gold sols were designed to determine both if gold in colloidal form could be floated, and also whether a film so produced would be reflective.

A gold sol was prepared according to the method of Zsigmondy.[20] A typical preparation was as follows: To 120 ml. of distilled water were added 7.5 ml. of a solution of 0.620 g. $HAuCl_4$ $3H_2O/100$ ml. H_2O and 9 ml. of 0.1M K_2CO_3. The mixture was heated to the boil with stirring, and 15 ml. of a solution of 3 ml. of 37% formaldehyde/1 1. were added. After a short boiling period a red translucent gold sol was produced.

All attempts to float the gold to the surface with standard flotation agents failed. Agents tried included isopropyl xanthate, potassium ethyl xanthate, Acintol FA (a fatty acid collector), and Aero Promoter 404 (mercaptobenzothiazole). In some cases a frother was also added.

The concentration of gold in the sol was varied from 0.05 g./l. to 1.43 g./l. The more concentrated sols flocculated on addition of the flotation agents. A sol prepared by the standard procedure and then dialyzed to remove electrolyte showed less tendency to flocculate, but still did not give flotation.

However, in most of the experiments a thin film of gold representing a very small fraction of the total gold present appeared at the surface at about the time that flocculation occurred. This film was brilliant gold in color and appeared to have a high reflectivity. To determine if the film consisted of a monolayer of contiguous gold particles or if aggregation somehow occurred to give a continuous patch of gold, it was floated off for examination by electron microscopy. A resin-covered copper screen was introduced and then gently withdrawn so that the patches of gold floated on top. Excess liquid was removed with filter paper and the specimen was gently flushed with several drops of water to remove soluble salts.

Figure 13 shows an electron photomicrograph taken at 40,000X.

It appears that the gold is in the form of single particles mostly between 600 and 800$\overset{\text{o}}{\text{A}}$ in size. The serrated outlines of the aggregates strongly suggest that they are made up of closely packed, individual colloidal particles. A macroscopic examination of gold patch on the resin-coated screen after drying revealed that it had lost its bright, golden luster and had become black. This is further evidence that the patch is composed of contiguous colloidal particles, since on removal of the liquid which carried the film the particles probably fell apart.

It therefore appears that the idea of floating a sol to give a reflective film is valid. The lack of success in floating the gold sol may not apply to the copper sol, since gold is probably too unreactive to enable the various flotation agents to work. If it should prove possible to prepare a copper sol in situ at the time of formation of the cloud and then float it, the method may have some promise. On the other hand, it may be difficult to prepare such a sol in situ in high enough concentration to be practical. If it is necessary to prepare the colloidal copper beforehand and use it as part of the package,

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it would seem to be more practical to go directly to the method of direct incorporation of copper film into a plastic matrix (to be discussed below) and avoid the difficulties of flotation.

4. Photochemical Reduction of Chelates

Some brief experiments were conducted to see if copper chelates dissolved in organic solvents could be photochemically reduced to form a copper film at the surface of the containing vessel. Copper acetylacetonate and the cupferron chelate of copper were dissolved in ethanol and chloroform and the solutions (in quartz tubes) were exposed to the intense ultraviolet radiant energy from a 6,000-watt xenon arc for three hours. No visible reaction occurred.

C. Incorporation of Evaporated Copper Film into Plastic

In view of the difficulties with the in-situ formation of copper film, it was decided to investigate the direct incorporation of previously prepared film into a plastic matrix. In a preliminary experiment, the interior of the bell jar of the vacuum evaporation unit was coated with cellulose acetate by depositing the acetate from an acetone solution. Copper was vacuum-evaporated onto the acetate, and then the acetate film was scored and removed from the bell jar. The film was dissolved in acetone, and the broken-up copper film was concentrated by centrifugation to 50% solids. The slurry of copper film was incorporated into a polyurethane foam formulation at a ratio of one part of copper to six of plastic, and foaming was allowed to proceed. The cell dimensions of the resulting foam were gross compared with the desired size of the spheres for the micro-balloons: the cell walls were 30-50μ thick, and the cell diameter about 300-400μ. Nevertheless, the sheets of copper film appeared to be well incorporated in the cell walls, and there was no noticeable folding, overlapping, or adhering of the films.

Two alternative approaches involving preformed metal film were considered: first, dispersal of free-standing metal film without any plastic or other support into the upper atmosphere, and second, preformation of metal film with a backing of plastic film and dispersal of this material, finely divided, into the upper atmosphere. Both of these approaches suffer from handling difficulties resulting from the use of finely-divided solids rather than fluids. By contrast, incorporation of preformed metal film

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into a prepolymer liquid would give a slurry which could be more easily handled. In addition, each of these approaches involves a specific difficulty. The free-standing metal film is an unstable substance because of its great amount of surface energy, and agglomeration and "welding" difficulties may be anticipated. Also, the combination metal and plastic film would give undesirable optical interference effects if the plastic film were of uniform thickness, as noted in an earlier section of this report.

III. COSTS   (Written by E. W. Pike, on the basis of information provided by Mr. H. W. Whitten of American Cyanamid Co., in reports and verbally.)

The major items of cost involved in the production of large quantities of plastic microballoons having the optical properties described in the previous sections, and wall thicknesses averaging 1μ are the colorant; and the generating device for converting the material, stored as two liquids, into separate airborne microballoons. The major development cost will be for the development of a compatible pair of resin formulation and generator, for the specific conditions of generation required in any specific application.

The National Metallizing Division of the Standard Packaging Corp. has presented the following estimates for the cost of Mylar film coated with an accurately controlled thickness of copper in the neighborhood of 0.02μ thick. As a function of the area ordered at one time, these estimated costs are:

$$10^6 \text{ ft}^2 \qquad \$0.025 - \$0.03 \text{ per ft}^2$$

$$10^7 \text{ ft}^2 \qquad \$0.022 - \$0.025 \text{ per ft}^2$$

$$10^8 \text{ ft}^2 \qquad \$0.008 - \$0.010 \text{ per ft}^2$$

A considerable period for the development and installation of special high-production machinery is included in the last of these estimates.

Roughly two hundred pounds of resin will make 10^6 ft^2 of reflecting surface; at roughly \$1/lb the cost of resin is negligible compared to that of the colorant.

The resin formulation and the generator must be developed compatibly; both are likely to vary considerably with the temperature and pressure of the atmosphere into which the microballoons are ejected, by the velocity (if any) of the generator with respect to the ambient atmosphere, and a number of other factors. Mr. Whitten has estimated the cost of developing a generator and a resin formulation compatible with generating 100 lb/sec of microballoons from an aircraft at relatively low altitude at roughly \$500,000, most of which is for pilot plant equipment and operation. These generator development

costs will be widely variable with the specific siutation, and with the precision with which optical and weight specifications must be held.

ACKNOWLEDGMENTS

REFERENCES

1. American Institute of Physics Handbook 6 105-6, New York, McGraw-Hill, 1957.

2. See, for example, Heavens, O., "Optical Properties of Thin Solid Films," New York, Academic Press, 1955.

3. R. C. Hall and J. P. Mickel, Inorganic Sytheses 5 82 (1957).

4. W. Biltz and P. Ehrlich, z. anorg. u. Allgem. Chem. 234 97 (1937).

5. H. Hahn and B. Harder, z. anorg. u. Allgem. Chem. 288 241 (1956).

6. I. Oftedal, z. physik. Chem. 134 301 (1928).

7. R. J. Heritage and J. R. Balmer, Metallurgia 47 171 (1953).

8. E. C. Marboe and W. A. Weyl, The Glass Industry 26 119 (1945).

9. V. Kohlschütter, Kolloid Ztschr. 12 285 (1913).

10. M. Volmer, Glastechn. Ber. 9 133 (1931).

11. F. Korosy, Nature 160 21 (1947).

12. A. Keller and F. Korosy, Nature 162 580 (1948).

13. V. Kohlschütter, Helv. Chim. Acta 13 980 (1930); 17 1097 (1934).

14. J. G. Maltby, Nature 160 468 (1947).

15. A. Angel and A. V. Harcourt, J. Chem. Soc. 81 1385 (1902).

16. C. Becue, Bull. Soc. Chim. France 1950 564.

17. V. P. Kornienko, Ukrain. Khim. Zhur. 18 579 (1952).

18. K. A. Hofmann and K. Schumpelt, Ber. 49 303 (1916).

19. A. Angel, J. Chem. Soc. 89 345 (1905).

20. R. Zsigmondy, Liebigs Ann. 301 30 (1898); Zeit. f. anal. Chem. 40 711 (1901).
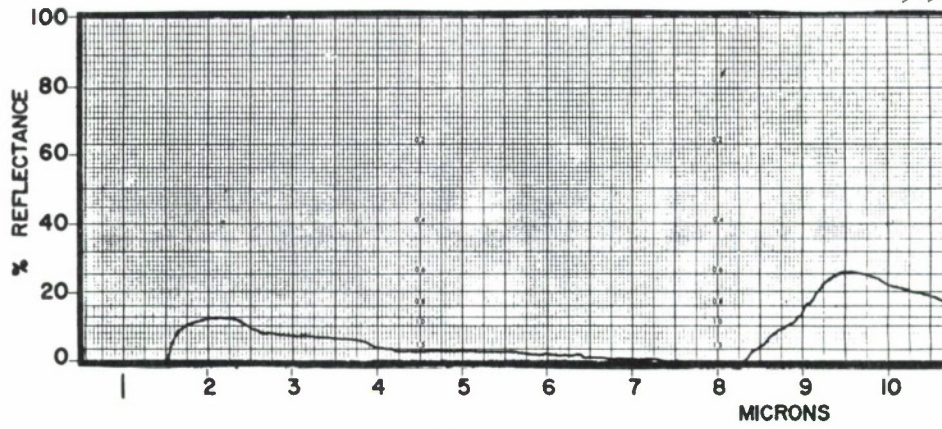
Figure 1a - Copper film, 13.3 mg. evaporated
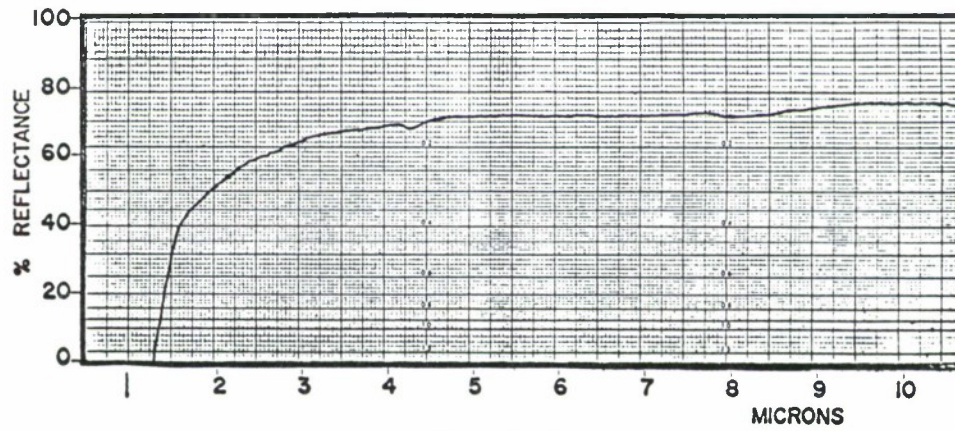
Figure 1b - Copper film, 27.2 mg. evaporated
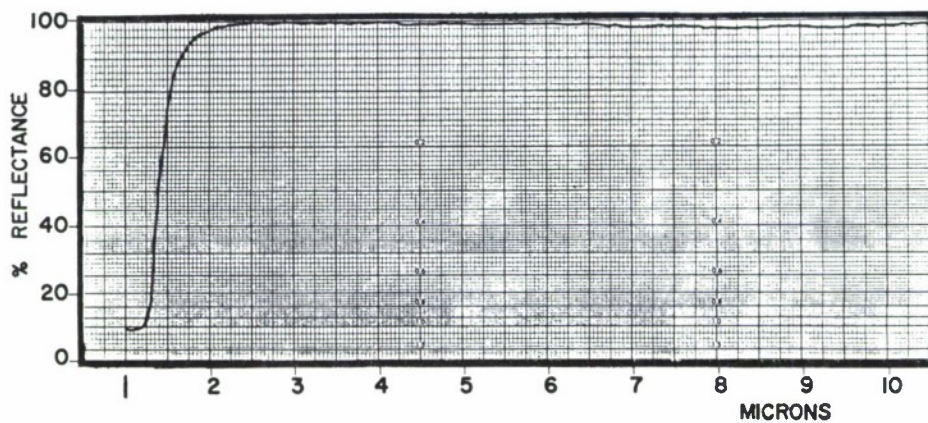
Figure 1c - Copper film, 55.8 mg. evaporated

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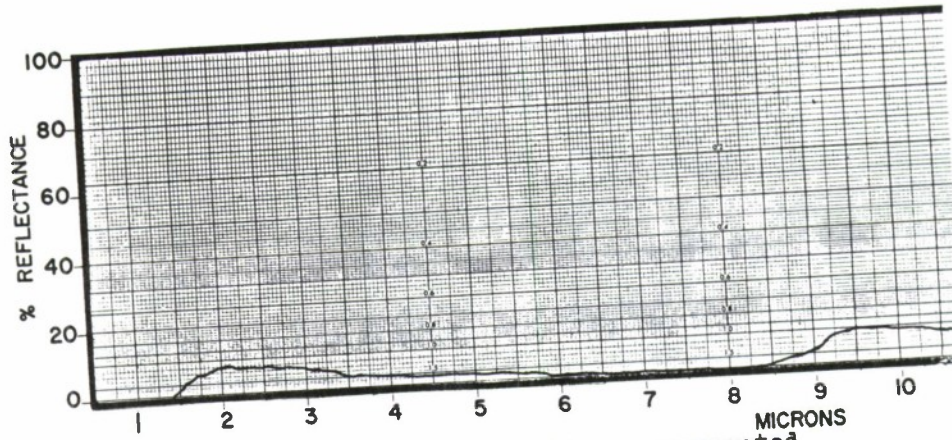
Figure 2a - Gold film, 26.1 mg. evaporated
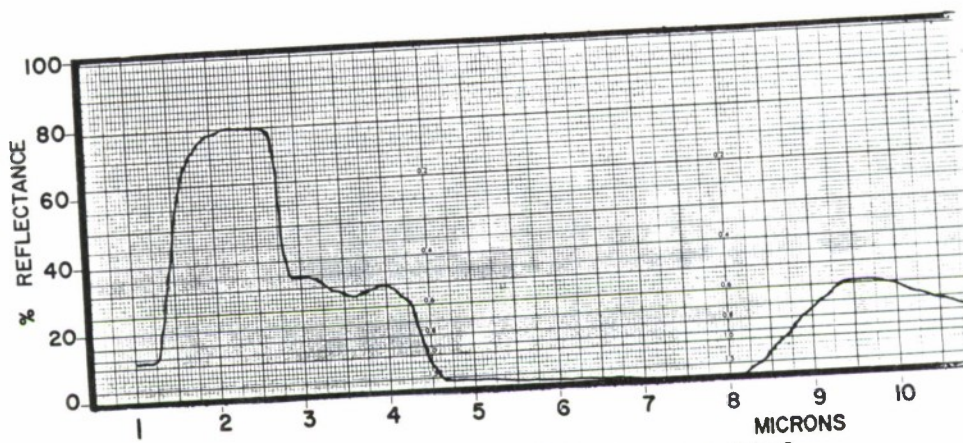
Figure 2b - Gold film, 58.6 mg. evaporated
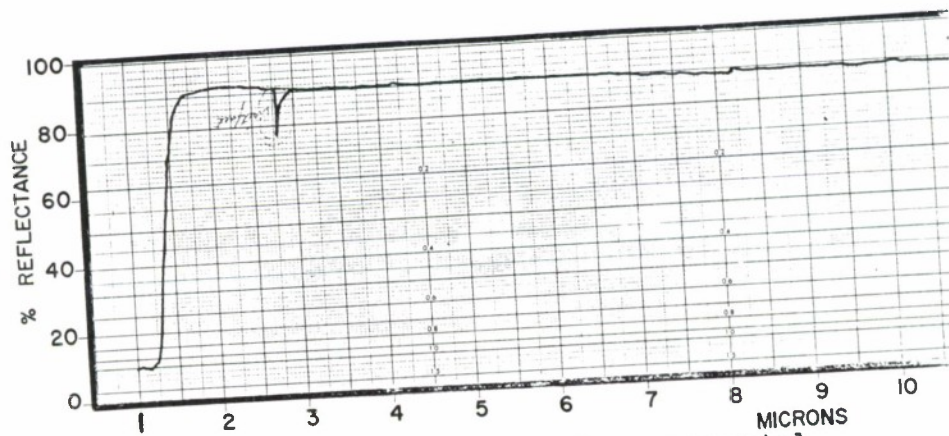
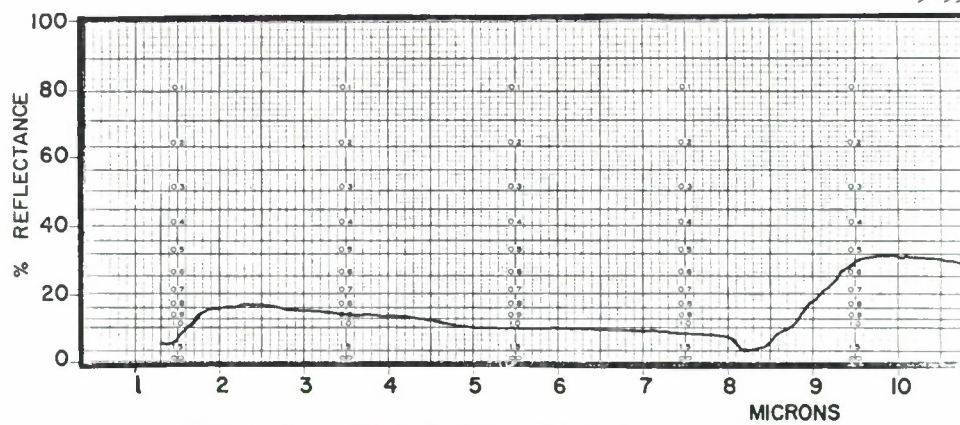Figure 2c - Gold film, 115.6 mg. evaporated
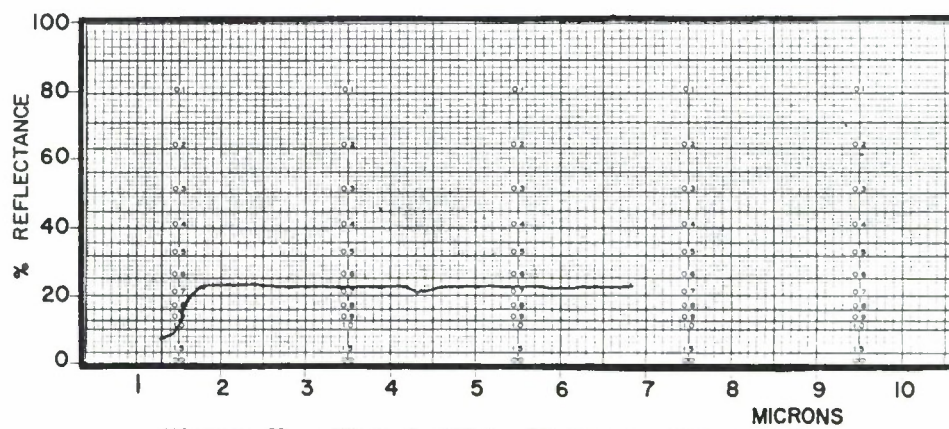
Figure 3a - Nickel film, 10.0 mg, evaporated
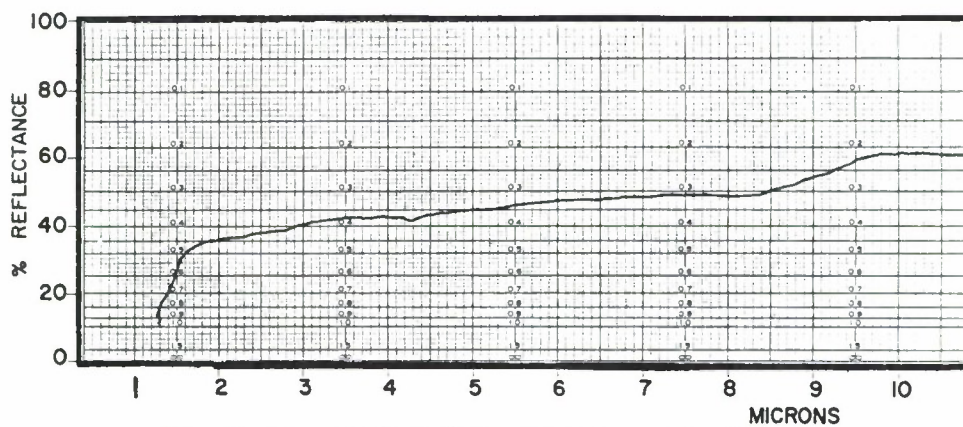
Figure 3b - Nickel film, 20.9 mg. evaporated
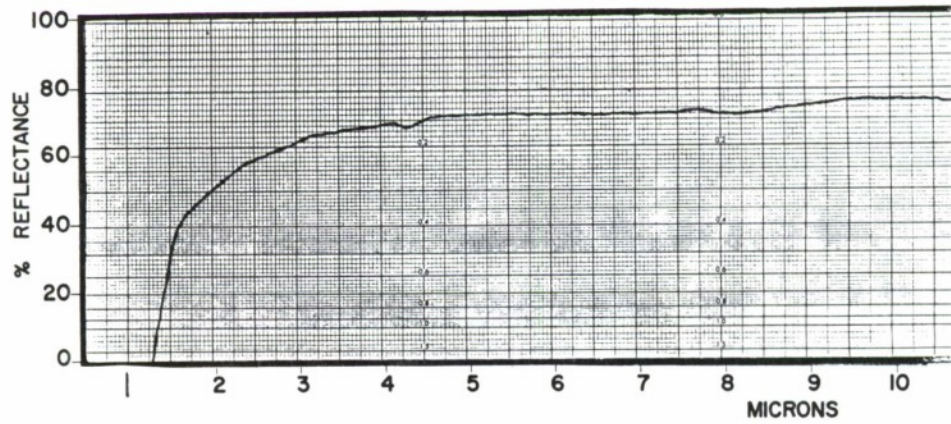
Figure 3c - Nickel film, 35.0 mg. evaporated

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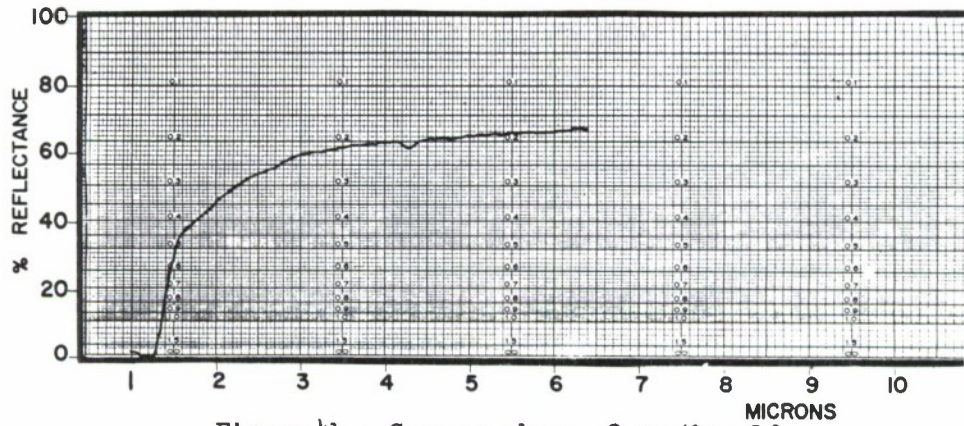
Figure 4a - Copper film shown in Figure 1b, freshly prepared

Figure 4b - Same as above, 2 months old
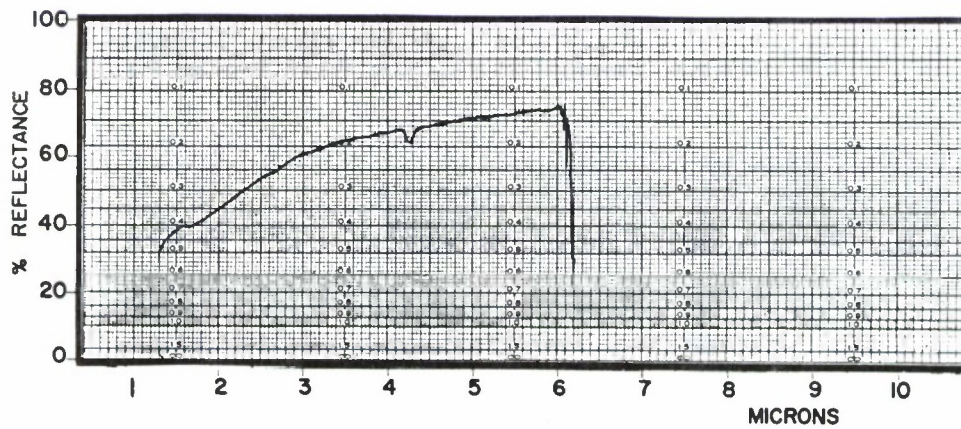
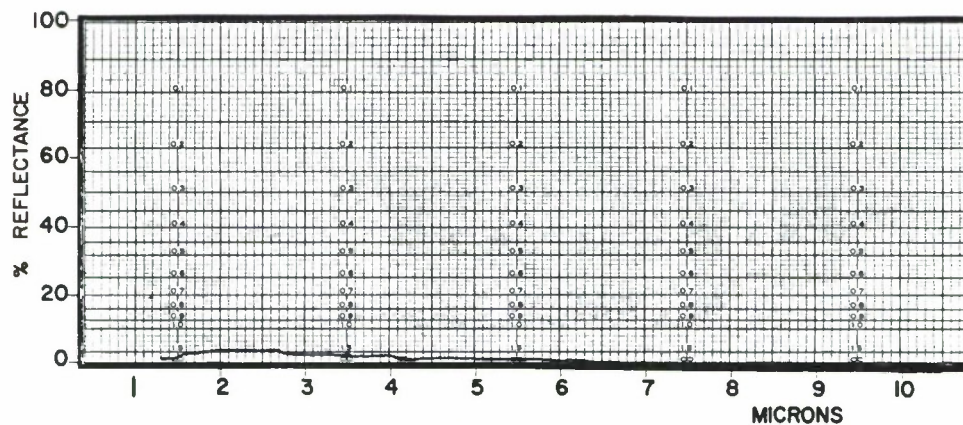Figure 4c - Same as above, 3 months old
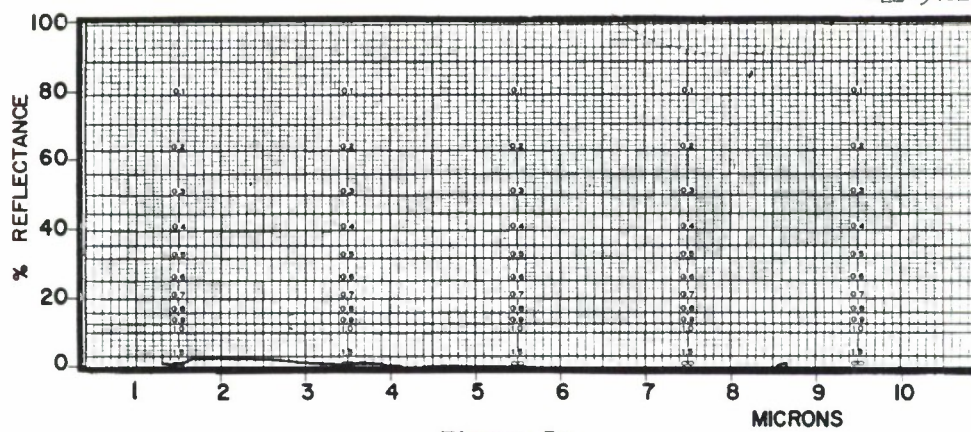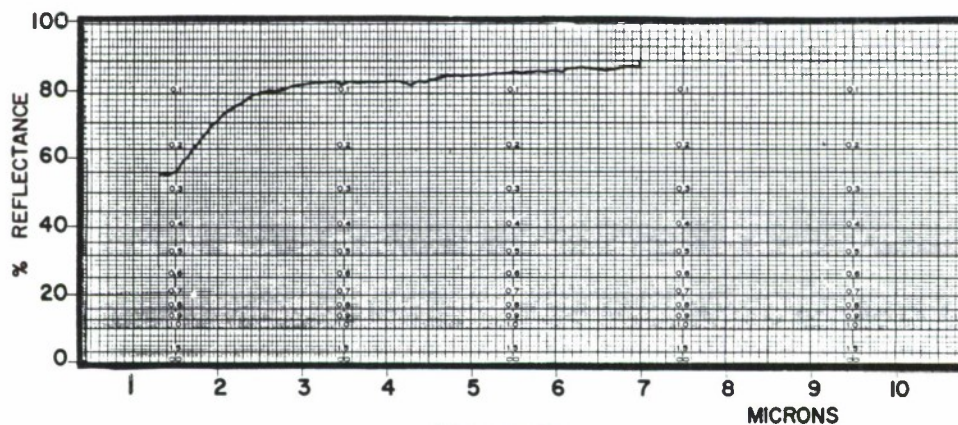
Figure 5a

Figure 5b

Figure 5c

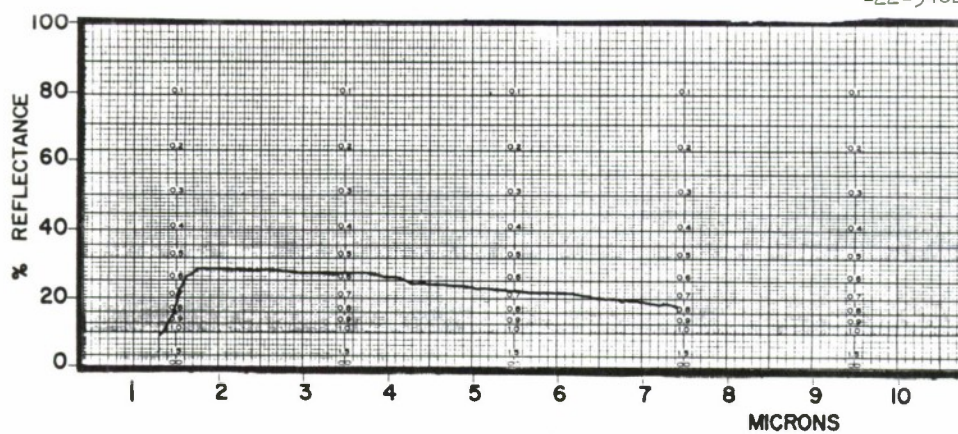Three copper films prepared on same day, 15 mg. evaporated
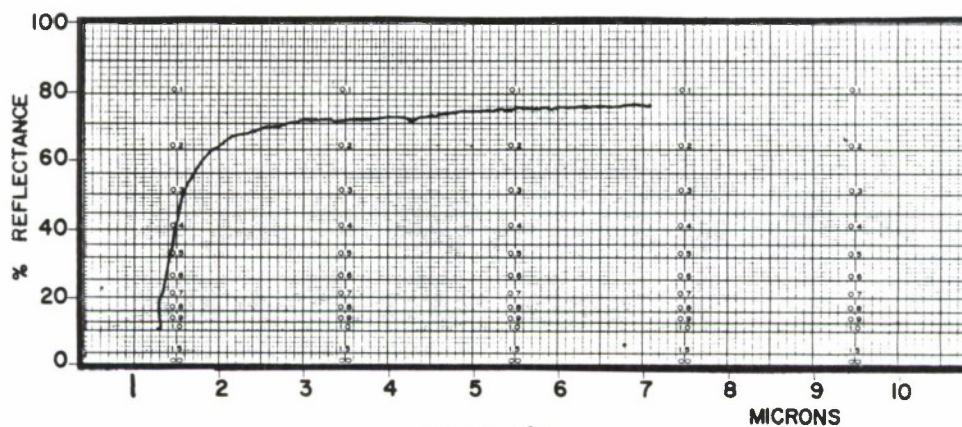
43
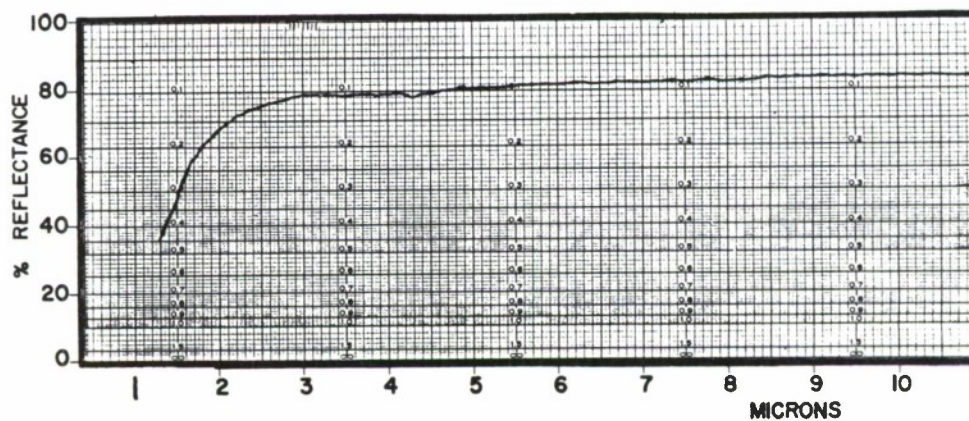
Figure 6a

Figure 6b

Figure 6c

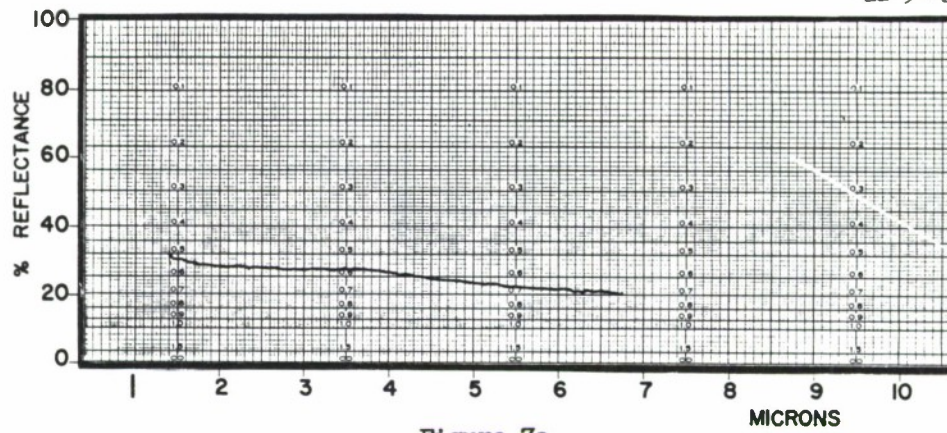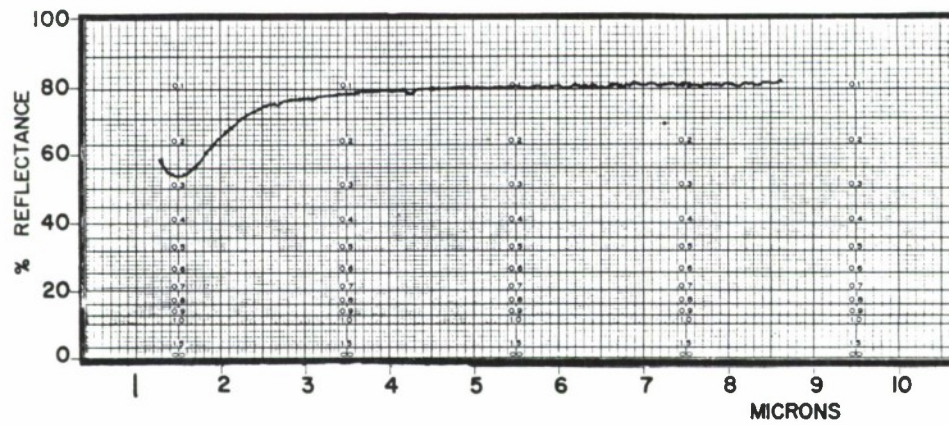Three copper films prepared on same day, 20 mg. evaporated

Figure 7a

Figure 7b
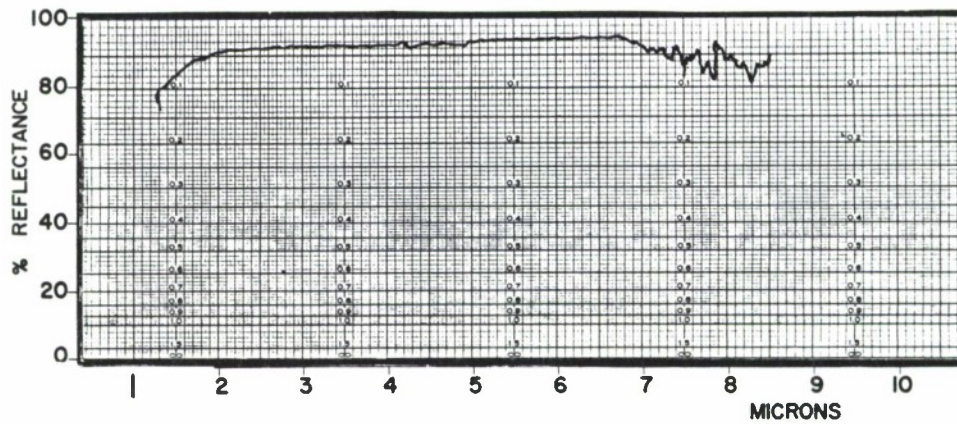
Figure 7c
Three copper films prepared on same day, 27 mg. evaporated

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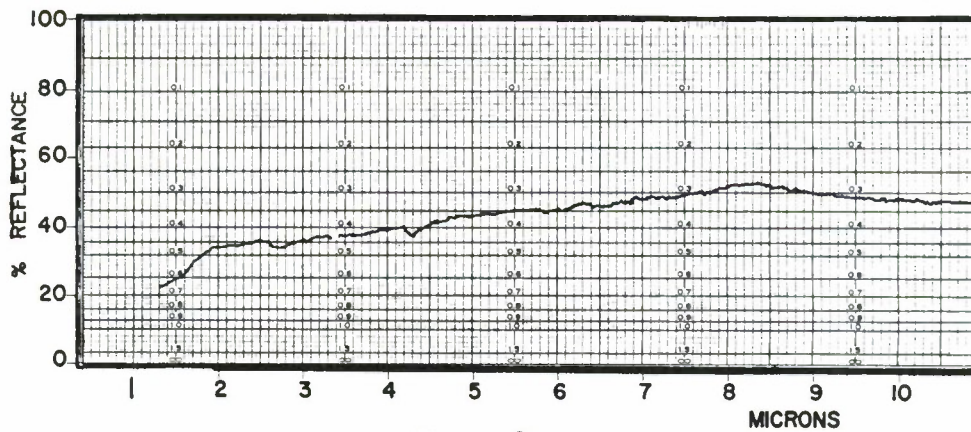
Figure 8a

Figure 8b

Films prepared by evaporation of titanium disulfide

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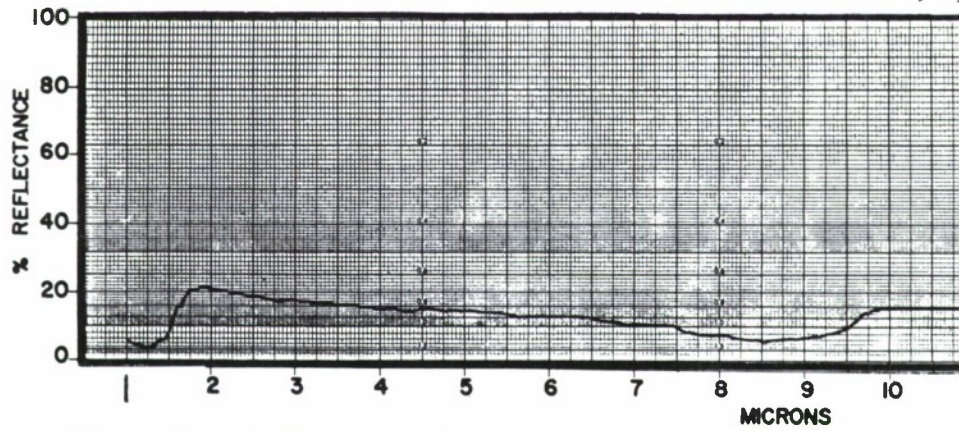
Figure 9a - Sn/Te semiconductor film, 25.0 mg. evaporated
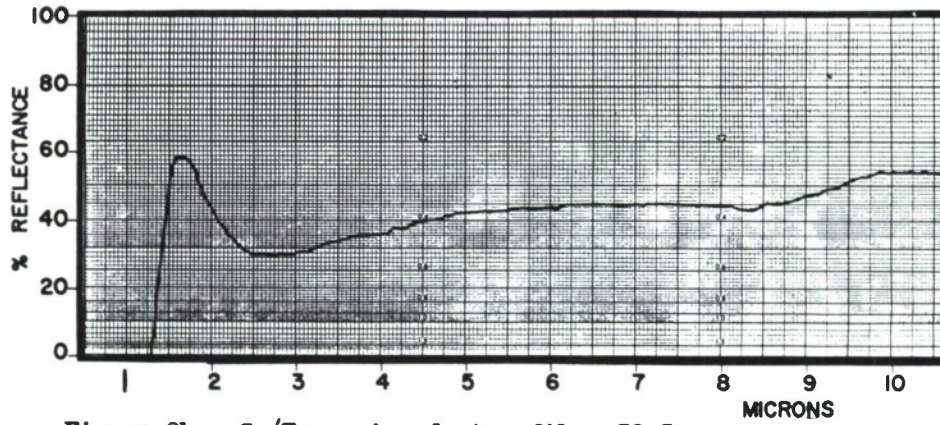
Figure 9b - Sn/Te semiconductor film, 52.5 mg. evaporated
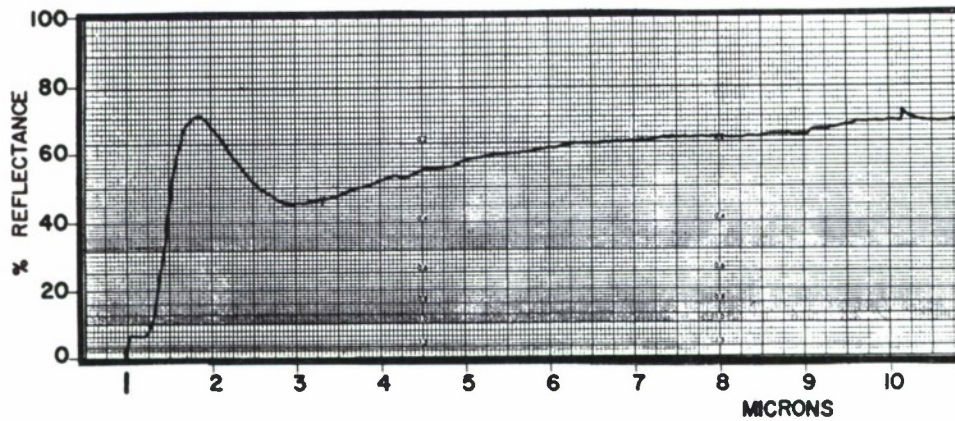
Figure 9c - Sn/Te semiconductor film, 107.0 mg. evaporated

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Figure 10 - Dependence of reflectance at 4μ
of copper film, 55 Å, on
thickness of plastic film

A - FREE STANDING FILM REFERENCE LINE

B - BACKED WITH PLASTIC

C - FACED WITH PLASTIC

THICKNESS OF PLASTIC FILM, μ

Figure 11 – Calculated Reflectance Curves
of Copper Film, 55 Å

A – FREE STANDARD FILM

B – BACKED WITH PLASTIC FILM, 0.6 μ

C – FACED WITH PLASTIC FILM, 0.6 μ

Figure 12 - Calculated Reflectance Curves
of Copper Film, 55 Å

A - FREE STANDING FILM

B - BACKED WITH PLASTIC FILM, 1.0 μ

C - FACED WITH PLASTIC FILM, 1.0 μ

Figure 13 - Electron photomicrograph of colloidal gold film

APPENDIX I

CALCULATION OF NORMAL REFLECTANCE OF A DOUBLE FILM

The normal reflectance of a double film bounded on both sides by air may be calculated by

$$R = \frac{cc^*}{aa^*}$$

where R is the normal reflectance, and c and a are matrix elements defined as follows:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} 1 & r_1 \\ r_1 & 1 \end{pmatrix} \begin{pmatrix} e^{i\delta_1} & r_2 e^{i\delta_1} \\ r_2 e^{-i\delta_1} & e^{-i\delta_1} \end{pmatrix} \begin{pmatrix} e^{i\delta_2} & r_3 e^{i\delta_2} \\ r_3 e^{-i\delta_2} & e^{-i\delta_2} \end{pmatrix}$$

In this equation, r_1, r_2 and r_3 are the Fresnel coefficients of reflection at the top of the first film, the bottom of the first film and the bottom of the second film, respectively. The quantities δ_1 and δ_2 represent the phase changes of the radiant energy in passing through the top and bottom films, respectively. For absorbing films, the Fresnel coefficients as well as the phase changes are complex, and stepwise calculation is resorted to.

A suitable stepwise program for the calculations is presented in the following equations:

Let n_1 and $k_1 \equiv$ the real and imaginary parts, respectively, of the complex refractive index of the film facing the incident radiant energy.

n_2 and $k_2 \equiv$ the same for the other film.

$d_1 \equiv$ thickness of the film facing the incident radiant energy.

$d_2 \equiv$ thickness of the other film.

$\lambda \equiv$ wavelength of the radiant energy being reflected.

We define the following quantities:

$$g_1 = \frac{1 - n_1^2 - k_1^2}{(1 + n_1)^2 + k_1^2}$$

$$h_1 = \frac{2 k_1}{(1 + n_1)^2 + k_1^2}$$

$$g_2 = \frac{n_1^2 - n_2^2 + k_1^2 - k_2^2}{(n_1 + n_2)^2 + (k_1 + k_2)^2}$$

$$h_2 = \frac{2(n_1 k_2 - n_2 k_1)}{(n_1 + n_2)^2 + (k_1 + k_2)^2}$$

$$g_3 = \frac{n_2^2 - 1 + k_2^2}{(n_2 + 1)^2 + k_2^2}$$

$$h_3 = \frac{-2 k_2}{(n_2 + 1)^2 + k_2^2}$$

$$\alpha_1 = 2\pi k_1 d_1 / \lambda$$

$$\gamma_1 = 2\pi n_1 d_1 / \lambda$$

$$\alpha_2 = 2\pi k_2 d_2 / \lambda$$

$$\gamma_2 = 2\pi n_2 d_2 / \lambda$$

$$p_2 = e^{\alpha_1} \cos \gamma_1$$

$$q_2 = e^{\alpha_1} \sin \gamma_1$$

$$r_2 = e^{\alpha_1} (g_2 \cos \gamma_1 - h_2 \sin \gamma_1)$$

$$s_2 = e^{\alpha_1} (h_2 \cos \gamma_1 + g_2 \sin \gamma_1)$$

$$t_2 = e^{-\alpha_1} (g_2 \cos \gamma_1 + h_2 \sin \gamma_1)$$

$$u_2 = e^{-\alpha_1} (h_2 \cos \gamma_1 - g_2 \sin \gamma_1)$$

$$v_2 = e^{-\alpha_1} \cos \gamma_1$$

$$w_2 = -e^{-\alpha_1} \sin \gamma_1$$

$$p_3 = e^{\alpha_2} \cos \gamma_2$$

$$q_3 = e^{\alpha_2} \sin \gamma_2$$

$$t_3 = e^{-\alpha_2} (g_3 \cos \gamma_2 + h_3 \sin \gamma_2)$$

$$u_3 = e^{-\alpha_2} (h_3 \cos \gamma_2 - g_3 \sin \gamma_2)$$

$$p_{12} = p_2 + g_1 t_2 - h_1 u_2$$

$$q_{12} = q_2 + h_1 t_2 + g_1 u_2$$

$$r_{12} = r_2 + g_1 v_2 - h_1 w_2$$

$$s_{12} = s_2 + h_1 v_2 + g_1 w_2$$

$$t_{12} = t_2 + g_1 p_2 - h_1 q_2$$

$$u_{12} = u_2 + h_1 p_2 + g_1 q_2$$

$$v_{12} = v_2 + g_1 r_2 - h_1 s_2$$

$$w_{12} = w_2 + h_1 r_2 + g_1 s_2$$

$$p_{13} = p_{12} p_3 - q_{12} q_3 + r_{12} t_3 - s_{12} u_3$$

$$q_{13} = q_{12} p_3 + p_{12} q_3 + s_{12} t_3 + r_{12} u_3$$

$$t_{13} = t_{12}p_3 - u_{12}q_3 + v_{12}t_3 - w_{12}u_3$$

$$u_{13} = u_{12}p_3 + t_{12}q_3 + w_{12}t_3 + v_{12}u_3$$

Then the normal reflectance of the double film, R, is given by

$$R = \frac{t_{13}^2 + u_{13}^2}{p_{13}^2 + q_{13}^2}$$

For a metallic film on a plastic substrate with the radiant energy incident on the metal side, n_1 and k_1 are the real and imaginary parts of the refractive index of the metal in film form, n_2 in the refractive index of the plastic, and $k_2 = 0$. The quantities d_1 and d_2 are the thicknesses of the metal and plastic films, respectively. If the radiant energy is incident on the plastic side, n_2 and k_2 are the optical constants of the metal film, n_1 is the refractive index of the plastic, and $k_1 = 0$. The quantities d_2 and d_1 are now the thicknesses of the metal and plastic films, respectively. For the case of the unsupported metal film, we take n_1 and k_1 as the optical constants of the metal film, d_1 as the thickness of the metal film, and set $n_2 = 1$ and $k_2 = 0$. The value of d_2 is immaterial, since this quantity cancels out in this case.

A Fortran program based on these equations is presented in Fig. I-1. The input quantities are explained by the following table:

Fortran Designation	Meaning
RRM	real part of refractive index of metal
RIM	imaginary part of refractive index of metal
RP	refractive index of plastic
DM	thickness of metal, $\overset{\circ}{A}$
DP	thickness of plastic, $\overset{\circ}{A}$
WAVEL	wavelength of radiant energy, $\overset{\circ}{A}$

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The program is designed to print out three quantities: first, the reflectance of the free-standing metal film; second, the reflectance of the metal film backed with the plastic film; and third, the reflectance of the metal film faced with the plastic film.

```
C     REFLECTANCE OF A COMBINATION METALLIC AND PLASTIC FILM
      E.ALLEN   -  NOV.6,1962
    5 ACCEPT 99,RRM,RIM,RP,DM,DP,WAVEL
      B1=RRM
      C1=RIM
      B2=1.
      C2=0.
      D1=DM
      D2=1.
      L=1
    4 G1=(1.-B1**2-C1**2)/((1.+B1)**2+C1**2)
      H1=2.*C1/((1.+B1)**2+C1**2)
      G2=(B1**2-B2**2+C1**2-C2**2)/((B1+B2)**2+(C1+C2)**2)
      H2=2*(B1*C2-B2*C1)/((B1+B2)**2+(C1+C2)**2)
      G3=(B2**2-1.+C2**2)/((B2+1.)**2+C2**2)
      H3=(-2.*C2)/((B2+1.)**2+C2**2)
      ALPH1=2.*3.14159*C1*D1/WAVEL
      GAM1=2.*3.14159*B1*D1/WAVEL
      ALPH2=2.*3.14159*C2*D2/WAVEL
      GAM2=2.*3.14159*B2*D2/WAVEL
      CG=COS(GAM1)
      SG=SIN(GAM1)
      EA=EXP(ALPH1)
      P2=EA*CG
      Q2=EA*SG
      R2=EA*(G2*CG-H2*SG)
      S2=EA*(H2*CG+G2*SG)
      EAN=EXP(-ALPH1)
      T2=EAN*(G2*CG+H2*SG)
      U2=EAN*(H2*CG-G2*SG)
      V2=EAN*CG
      W2=-EAN*SG
      CG2=COS(GAM2)
      SG2=SIN(GAM2)
      EA2=EXP(ALPH2)
      EAN2=EXP(-ALPH2)
      P3=EA2*CG2
      Q3=EA2*SG2
      T3=EAN2*(G3*CG2+H3*SG2)
      U3=EAN2*(H3*CG2-G3*SG2)
      P12=P2+G1*T2-H1*U2
      Q12=Q2+H1*T2+G1*U2
      R12=R2+G1*V2-H1*W2
      S12=S2+H1*V2+G1*W2
      T12=T2+G1*P2-H1*Q2
      U12=U2+H1*P2+G1*Q2
      V12=V2+G1*R2-H1*S2
      W12=W2+H1*R2+G1*S2
      P13=P12*P3-Q12*Q3+R12*T3-S12*U3
      Q13=Q12*P3+P12*Q3+S12*T3+R12*U3
      T13=T12*P3-U12*Q3+V12*T3-W12*U3
      U13=U12*P3+T12*Q3+W12*T3+V12*U3
      REFL=(T13**2+U13**2)/(P13**2+Q13**2)
      PRINT 99,REFL

      GO TO(1,2,3),L
    1 L=2
      B2=RP
      D2=DP
      GO TO 4
    2 L=3
      B1=RP
      C1=0.
      B2=RRM
      C2=RIM
      D1=DP
      D2=DM
      GO TO 4
    3 PRINT 99
      PRINT 99
      GO TO 5
      END
```

Figure I-1 - Fortran program for thin film reflectivity calculations

SPECIAL CERAMIC MATERIALS

Final Report

to

Lincoln Laboratory

from

Corning Glass Company, Research Laboratories

Project Manager, Mr. T. J. McAvoy

I.   TIN OXIDE FILMS

A.   Background

Thin oxide films usually of iron or tin have been used as a decoration for vitreous surfaces for many years. The iridescent finish caused by interference effects in these films is reminiscent of the iridescent surface of weathered ancient glass. The technological application of tin oxide films began around 1928 when Littleton (of Corning Glass Works) used a high resistivity film of tin oxide to supress corona on high tension insulators (U. S. 2, 118, 785). Subsequently a very extensive patent literature in conducting oxide film developed, the films having found many practical applications as transparent conductors, heating elements, infrared reflectors and in oxide film resistors.

During this period of material development it was discovered that certain additives to the pure SnO_2 film have desirable effects on its electrical and optical properties. Notable among these additives are antimony (J. M. Mochel, U. S. 2, 522, 531 to Corning Glass Works) which improves the stability and lowers the temperature coefficient of resistivity of SnO_2, and fluorine (W. O. Lytle and A. E. Junge, U. S. 2, 566, 346 to Pittsburgh Plate Glass Co.) which provides a SnO_2 film with low resistivity and high visible transmittance.

B.   Preparation

Stannic oxide films can be formed by the pyrolysis-hydrolysis of a vapor containing tin chloride and water on a substrate at temperatures above $450^{\circ}C$.

They are commonly made by simply atomizing an aqueous solution of stannic chloride onto a hot substrate in the practical temperature range of 500 to $800^{\circ}C$. The amount of stannic oxide deposited under practical conditions is of the order of 1% of the total amount sprayed. Anhydrous stannic chloride vapor can be used, the moisture for hydrolysis coming from the carrier gas. Although more sophisticated techniques of application can be used, surprisingly, the relatively crude method·of direct atomization on the hot substrate has in practice proved to be generally more practical and reproducible.

As noted above, there are only two known dopants which give a marked enhancement of electrical conductivity and infrared reflectivity along with reasonably stable electrical characteristics; these are fluorine and antimony. Fluorine is usually added to the coating solution as aqueous hydrofluoric acid or ammonium fluoride; antimony may be added as either the trichloride or the pentachloride. Other dopants reported in the literature have been boric oxide and phosphoric oxide but the effect of these fall short of the two noted above.

Control of dopant concentration depends on the physical chemistry of the system involved. For example, the amount of antimony going into the film is proportional to the concentration present in the spray solution. The amount of fluorine going into the film is pretty much independent of concentration in the spray solution, at least above a certain low level, but it is probably influenced by temperature. On the basis of electron density, it can be calculated that about 0.4 mol% of fluorine is present in the lattice.

C.   Electrical Characteristics

In the pure tin oxide film (or crystal) there is usually an oxygen deficiency, the amount of which is dependent on the thermal history and the accompanying effective ambient oxygen activity. This occurs probably because the perfect SnO_2 lattice is under a packing strain; energy considerations therefore favor vacant oxygen sites to relieve the otherwise tight packing. With each oxygen vacancy there are associated two electrons which may be available to participate in electric current flow. These vacancies, however, constitute a potential well in the crystal field which act as trapping centers, limiting both mobility and free electron concentration.

When this oxygen site is occupied by the smaller fluorine ion, one electron remains. The trapping effect of the ionized fluorine is very weak, therefore, more electrons are free and their mobility is higher.

When the tetravalent tin ion is replaced by the smaller pentavalent antimony ion, the relaxation of strain permits oxygen sites to be filled and a conduction electron is available from the antimony ion, the net result being minimal electron trapping and

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and increased mobility.   Following is a table of data typical of the films discussed:

Film	Resistivity ohm-cm $\times 10^{-3}$	Carrier Density $\times 10^{20}$	Electron Mobility $cm^2/sec/volt$
pure SnO_2	8.3	0 59	12.8
SnO_2 + 1% Sb	.50	5.8	20.8
SnO_2 + 2% Sb	.60	7.4	13.2
SnO_2 + 4% Sb	1.9	7.3	4.52
SnO_2 + F	.39	7.5	21.4

D.   Optical Properties

For a particular dopant system there is a marked correlation between the electrical resistivity of a tin oxide film and its infrared reflectivity.   Of course, for a given composition, there is a direct correlation of reflectivity with film thickness.

With reference to the problem at hand, the following criteria were used in selecting a film system:

a)   high reflectivity at 4.3 microns and relatively low reflectivity at 2.7 microns, the ratio of reflectivity at 4.3 to 2.7 to fall between 0.5 and 0.7.

b)   minimal reflectivity and absorptivity in the visible region.

c)   maximum reflectivity at 4.3 microns per unit weight per unit area of film --- this has been tentatively evaluated as R at 4.3 microns/thickness.

After searching through a number of tin oxide film systems, the fluorine doped and antimony doped films were selected for further study.   Films were prepared in varying thicknesses on glass plates and measured for absorption and reflectance.   Results are as follows:

Coating Solution (Std. Soln.* plus dopants listed)	Coating Temperature	Interference Reflection Order	Color	Thickness Å	% Reflectance R_1 2.7	at R_2 4.3	Ratio R_1/R_2	Figure of Merit x 10^{-2} R_2/t
3% HF, 3% isopropanol	650°C	1	red	800	22	35	.63	4.4
"	"	2	blue	1770	40	56	.71	3.2
"	"	2	yel	2180	48	65	.74	3.0
"	"	2	red	2440	45	64	.70	2.6
"	"	3	yel	3610	56	74	.74	2.05
"	"	3	red	4070	62	78	.79	1.9
9% HF, 3% isopropanol	700°C	3	red	4070	39	61	.64	1.5
"	700°C	3	red	4070	60	73	.82	1.8
1% SbCl$_3$	650°C				31	44	.64	
"	650°C				60	73	.82	

* Standard solution contains 1 gram of $SnCl_4 \cdot 5H_2O$ per ml of 16% HCl.

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The antimony doped system is included in the table simply for comparison -- it must be rejected because of its absorption in the red end of the visible region (and consequent blue color.) Reflectance at 4.3 and 2.7 microns is plotted against film thickness for the fluorine-doped system in Fig. 1. An examination of Fig. 1 shows that the maximum ratio of R at 4.3 to film thickness is achieved for the 1st order red film at about 800$\overset{o}{A}$. From the table it can be seen that this film also has a low ratio R_1/R_2, well within the 0.5 to 0.7 limits originally set. Two other interesting points can be derived from the table: (a) changes in the temperature of deposition and the HF concentration affect the ratio R_1/R_2 but do not drastically change the R_2/t ratio and (b) for a particular value of R_2 (the reflectance at 4.3 microns) the ratio R_1/R_2 is higher for the antimony-doped film than for the fluorine-doped film.

As a result of these measurements, it was decided to prepare flakes of the 1st order red fluorine-doped film for evaluation. One problem with this 800$\overset{o}{A}$ thick film is that it is much more affected by surface imperfections in the substrate than a thicker film. Hence, one might expect more visible light scattering from the thin film. In view of this problem, it was also decided to prepare a sample of flakes from a 3rd order red film (4070$\overset{o}{A}$ thick).

E.   Preparation

As described in the proposal of January 10, 1962, a possible method of preparing thin flakes of SnO_2 of uniform thickness would be to deposit the film so that it could be readily removed from the substrate. To this end, several types of soluble substrate layers to enable stripping of the SnO_2 film by water or solutions were tried, namely:

a)   Fused Salts:

20% $BaCl_2$, 78% Na_2CO_3, 2% $NaCl_1$, mp 562°C

KCl-NaCl eutectic mp 560°C $BaCl_2$-$CaCl_2$ eutectic mp 600°C

b)   Fused Glasses:

B_2O_3 mp 577°C
$NaPO_3$ mp 625°C

c)   Films (pyrolyzed)

ZnO

La_2O_3

d)   Rock Salt Plates

In general, on applying the tin oxide film, the fused salts immediately crystallized with a grainy surface which gave such a rough surface to the overlying film that they no longer showed interference color or had the desired optical properties.

No film would form on the B_2O_3 glass, apparently because the film would not nucleate on this surface. Film formed readily on the molten $NaPO_3$ surface; wrinkling occurred during cooling, but on a much larger scale than the film flake size required. Electrical measurements on the films on $NaPO_3$ showed them to be the correct composition.

The zinc oxide surface also receives a good film of SnO_2, except that there is apt to be a small amount of roughening due to crystallization in the substrate film after it is formed.

The films on rock salt were made principally for I.R. transmissions, but were poorly adherent and cracked up.

These "parting agents" were first applied to substrates of various materials to act as supports or carriers. Among those tried are Code 7740 glass, platinum, aluminum, copper, Nichrome, stainless steel, nickel and Code 9608 glass-ceramic.

Platinum is a very good substrate, but in thin sheet it buckles and coats very unevenly.

Aluminum at 600° lies flat against the hearth, but its oxide cannot be separated from the tin oxide film.

Copper oxidizes very badly in spite of the phosphate glass coating.

Nichrome and stainless steeel give an insoluble scale for oxidation, probably a chromite, which is resistant to strong reagents at boiling temperatures.

Nickel gives some oxidation residue, but it can be removed from the SnO_2 flakes by strong acid solution in a final washing after a large batch of flakes have been collected.

7740 glass and 9608 glass-ceramic substrates have their entire surfaces spalled off by the sodium phosphate glass layer, and are therefore usable only once.

Thin fired-on metal films of both gold and platinum on a glass base have also been tried both as substrates for tin oxide and as substrates for soluble layers but without any particular advantage.

The combination chosen for further work is rolled nickel plate with a layer of sodium metaphosphate glass fused on. This is coated at a temperature of 650°C for both the phosphate layer and the tin oxide film.

11.   PILOT MANUFACTURING OPERATION

To provide samples of tin oxide flakes for further evaluation and to determine the feasibility of manufacturing such flakes on a large scale, a pilot manufacturing operation was established. The general process used is as follows:

> Nickel sheets 1' square and . 125" thick were coated
> with a layer of powdered "sodium hexametaphosphate",
> then placed on a continuous constant speed lehr belt
> which brought them to a temperature of 650°C. At
> this temperature the phosphate melts to a smooth
> viscous layer. In the apparatus used here, the lehr
> belt speed was 24"/minute, the lehr having a thermal
> gradient with peak of 665°C with 650°C in the region
> of the coating operation.

The coating solution was sprayed onto the phosphate coated plates by an atomizer oscillating so as to scan each 12" plate about 60 times.

Two coating solutions were used: for the 3rd order red film a standard solution of 1 gm. $SnCl_4 \cdot 5H_2O$ per ml of 16% HCl plus 3% HF; for the 1st order red film, the above solution was diluted 1:3 with 20% HCl solution. The setting of the atomizer, scan and lehr belt rates and solution concentrations can be adjusted to give the desired film thickness. Thickness was checked periodically by running a Code 7740 plate through the lehr.

As the coated nickel plates came out of the lehr, they were dipped into a cold water bath for about 10 seconds to spall off as much of the film as possible, after which

they were stacked vertically in a water tank to soak off the phosphate glass. This sudden quenching of the plates caused warping which was straightened out before running them through the process again. For one part of the run, steam at 15# gage pressure was used to clean the hot nickel plates. This technique showed promise: it removed the SnO_2 film without stripping off the phosphate layer, thus allowing the phosphate to be used again. Incidentally, when the nickel plates come out of the lehr, the phosphate coating is soft --- like taffy; it can be scraped off with a spatula.

The combined "sludge" removed from the nickel contains sodium metaphosphate glass and corrosion products of the nickel, in addition to the desired SnO_2 flakes. Most of the phosphate was removed from the SnO_2 by soaking in water --- about 6 changes of water were made in the present experiments. The residue was then soaked in aqua regia for 6 hours to remove all foreign matter from the tin oxide (which is very insoluble). After three more washings in water and two in methyl alcohol, the tin oxide powder was dried in air and stored. Undoubtedly this clean-up process could be done more efficiently but we wanted to get the cleanest product possible in the first experiments.

Putting 24 nickel plates through the cycle at a time, the above experiments required two men for about an hour, with about 2 days required of clean-up involving the intermittant attention of one man. For a run of 200 plates which yields 14 grams of tin oxide, the direct production cost as described above is about \$12/gram. By optimizing the above process it should be possible to bring production cost down to about \$3/gram not inclusive of capital equipment costs.

III.   LARGE SCALE PROCESSES FOR FORMING TIN OXIDE FLAKES

There is really not much point in estimating in any detail the cost of scaling up this process, since it obviously is only suitable for small scale operation. As noted in Dr. E. W. Pike's letter to T. C. MacAvoy (11 July 1962), there is really no need to confine the process to the deposition of tin oxide films onto flat substrates --- flakes which are curved would be satisfactory so long as the radius of curvature is at least a few times larger than the longest wavelength of interest. It should therefore be possible to get good flakes by depositing on a substrate with a radius of at least 15 microns.

All that is required for the deposition of a suitable tin oxide film is that (a) sufficient energy be available at the substrate surface to make the hydrolysis reaction rapid on the surface (while slow in the vapor) and (b) that nucleation be rapid. From our past experience it is known that deposition on powders or fibers is poor unless sufficient heat is supplied to the reaction chamber with the powder or fiber. This has been done and we have, in the past, developed methods for coating, for example, glass powder and fiber glass cloth with SnO_2 films.

Although it is not possible to undertake further experimental work along these lines under the present contract, a number of possible approaches can be envisioned:

a) Streams of molten sodium phosphate could be run from a multi-holed spinnerette through an $SnCl_4$-H_2O vapor mixture and thence into water, the dwell time in the vapor being adjusted to give the proper SnO_2 film.

b) Streams of molten phosphate could be run into alcoholic or acid (HCl) solutions of suitable tin compounds to give the desired film. In the case of acid solution, concentrations could be adjusted to give films and then dissolve out the phosphate.

c) Finely powdered sodium metaphosphate could be converted to hot, soft glass spheres by blowing through flames or hot tubes. The hot spheres could then be blown into a reaction chamber filled with $SnCl_4$-H_2O vapors for the film forming operation. The coated spheres would be collected by a dust separator and processed in hot dilute acid to recover the SnO_2 film. A process very similar to this has been developed at Corning for coating glass powders. Many variations of this process can be envisioned; process equipment is available from spray drying and catalyst production process.

Without pursuing this "estimation" further, it can readily be seen that techniques are available from standard chemical production practice for the production of tin oxide flake materials at a cost considerably lower than the $3/gram estimated for the process used in our experiments. A cost of a little over $.01/gram would put it in the range of boron fuels, a cost which is within the realm of practicability after the diligent

application of a large amount of chemical engineering. Even with 100% utilization of the $SnCl_4$ reagent, it seems unlikely that the cost of SnO_2 flakes will ever be lower than $1/pound.

IV.   SAMPLES PROVIDED WITH THIS REPORT

As described above, it was decided to prepare a sample of the 1st order red which is about 800Å thick. About 5 grams of this material was recovered (this is equivalent to a little over 100 square feet of film surface) and is submitted with this report. A second run was made and resulted in about 10 grams more of flakes graded in thickness from about 1st red to 2nd yellow (2180Å) plus a sample of 3rd red (4070Å). All of these samples have been included and are appropriately labeled. We have also prepared and submitted for evaluation a sample of the same film composition deposited in graded thickness from 800Å to about 5000Å on a Code 7740 glass plate. The various color orders have been marked; thicknesses can be found using the table on page 6 of this report.

In the proposal, the possibility of coating the individual flakes with a deflocculating agent such as stearic acid to improve the dispersal of the flakes on ejection from a package was considered. We have developed methods for coating fine powders with ammonium stearate followed by conversion to stearic acid by mild heating. Similar processes could without doubt be applied to the SnO_2 flakes. Since the sample size is limited, however, and optical properties are of interest, it was decided not to coat the flakes with stearate.

It had also been planned to prepare the flakes at about 4 to 6 microns in diameter. The size of the flakes in the samples submitted varies from 40 to 200 microns with an average of about 120 microns as determined by optical microscopy (photomicrograph

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* This sample is available for examination, and small quantities will be supplied for study as long as the supply lasts. Write to E. W. Pike, M. I. T. Lincoln Laboratory, Lexington 73, Massachusetts 02173.

submitted with report to Lincoln Labs.) They can probably be milled to a smaller average size but it was decided not to tamper with them until after they had been evaluated.

V.   CONCLUSIONS

As a result of this feasibility study it can be concluded that;

a)   The optical objectives set out in the introduction to this report can be met by suitably doped tin oxide films.

b)   Tin oxide films can be prepared in flake form by deposition on a soluble substrate followed by washing with the appropriate solvent.

c)   On the basis of relatively crude preliminary experiments it is possible to prepare tin oxide flakes on a modest scale for about $3/gram.

d)   Reasonable conjecture leads to the conclusion that tin oxide flakes could be prepared for a few dollars per pound in a process which depends on powdered substrates and large scale continuous equipment.
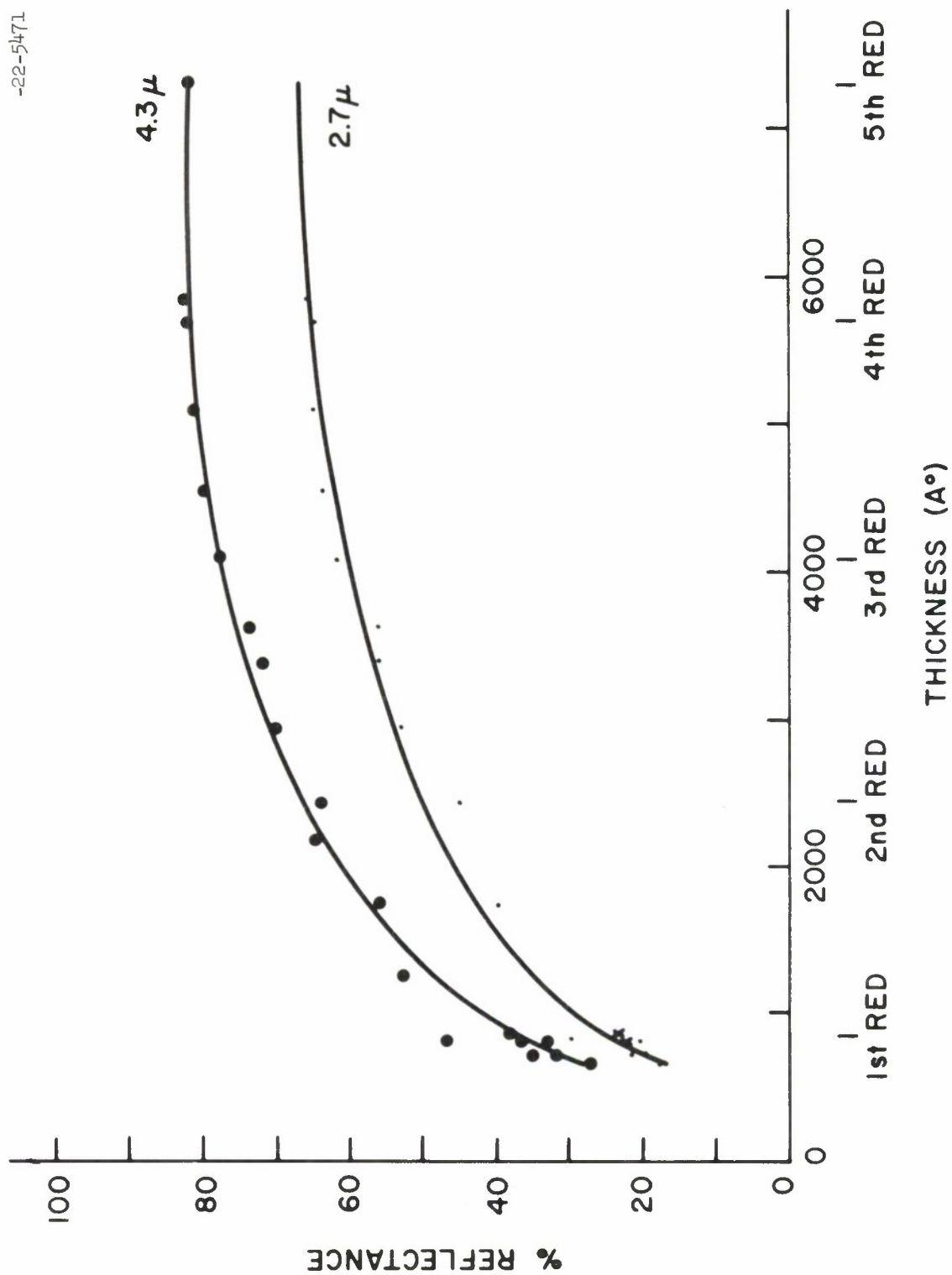
Figure 1 - Reflectance of SnO_2:F film vs thickness

72
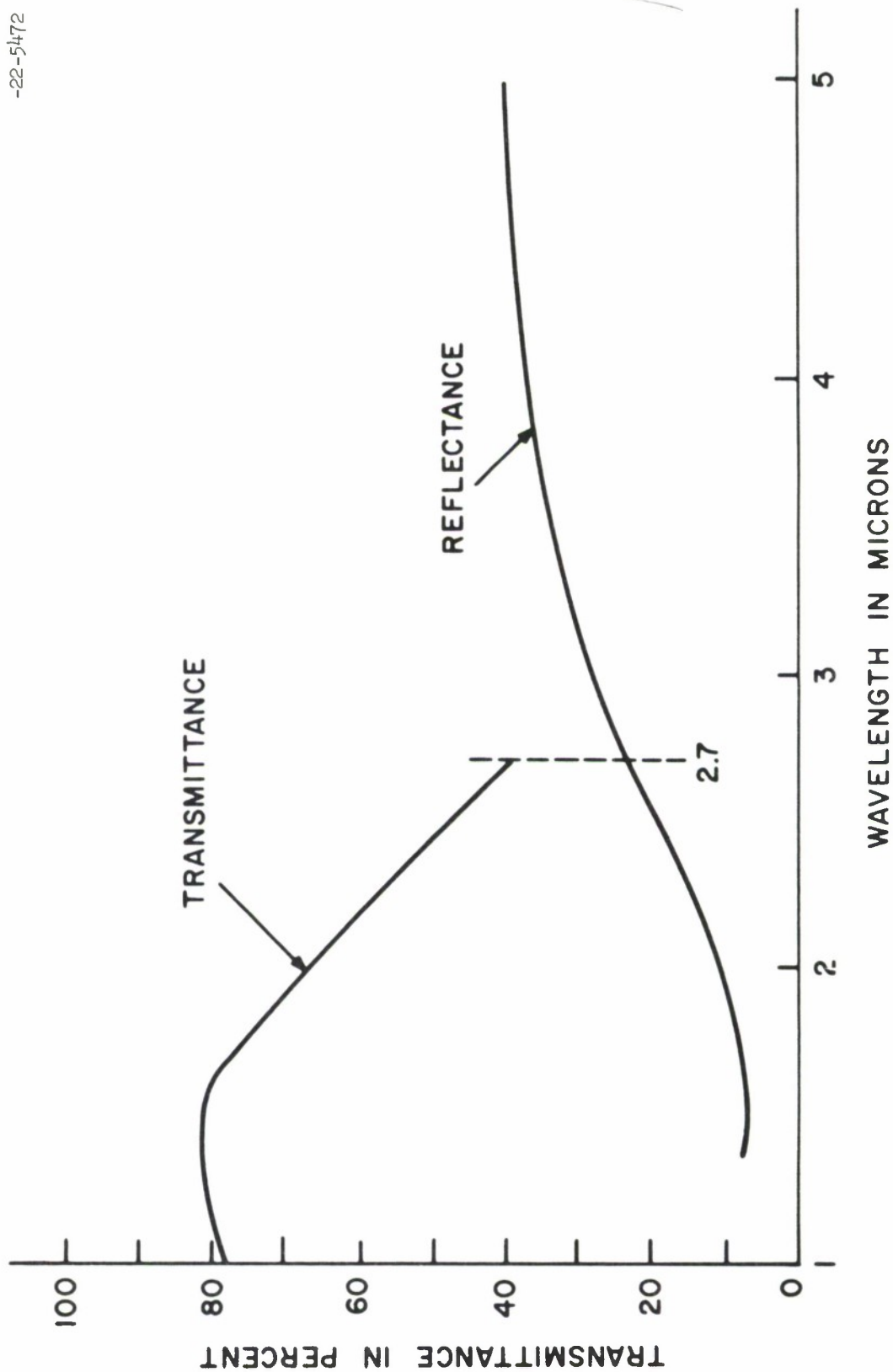
Figure 2 - Optical properties of SnO_2 film approximately 1000A° thick

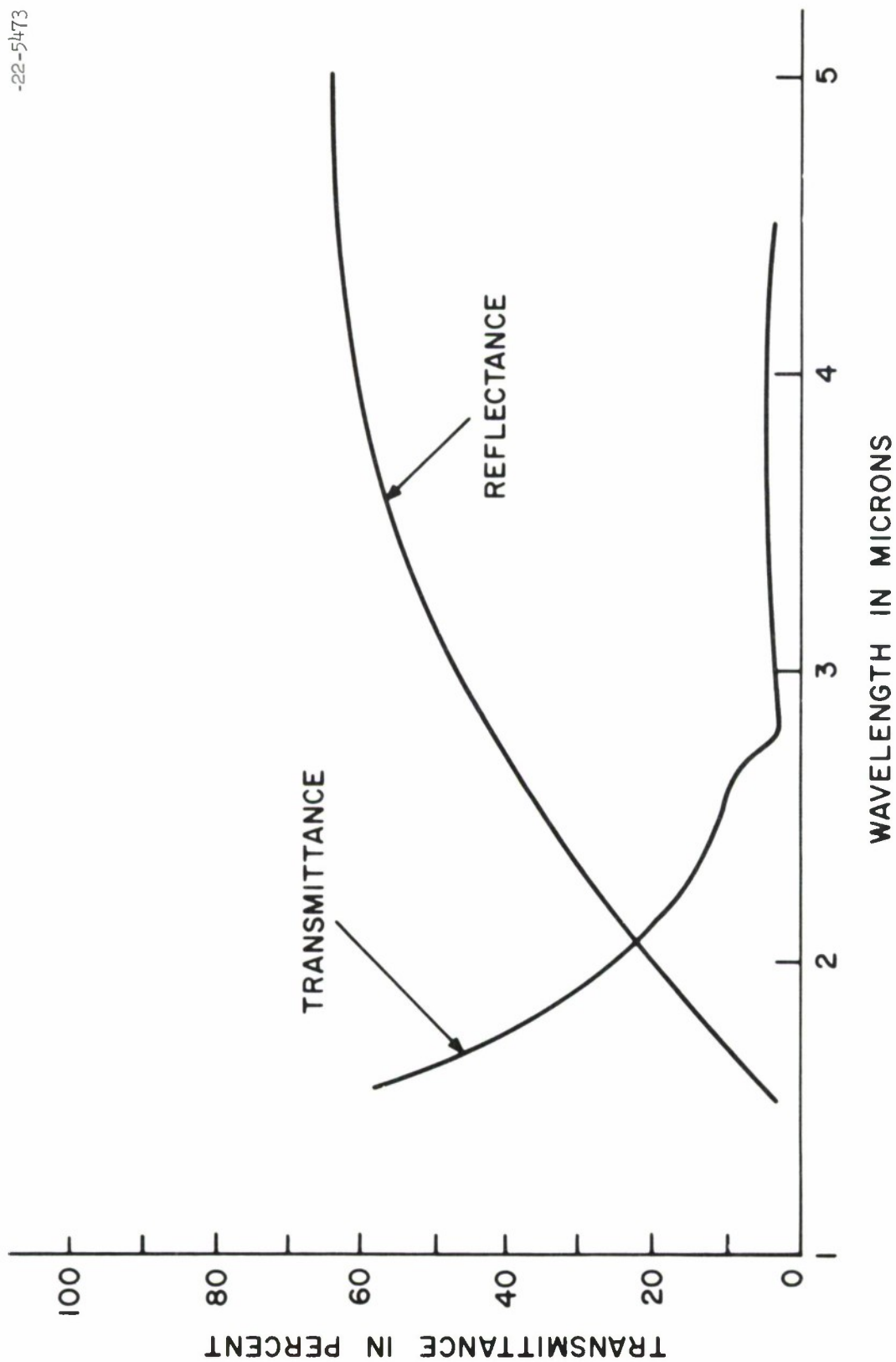Figure 3 - Optical properties of SnO_2:F film approximately 2000A° thick

100 µ

Figure 4

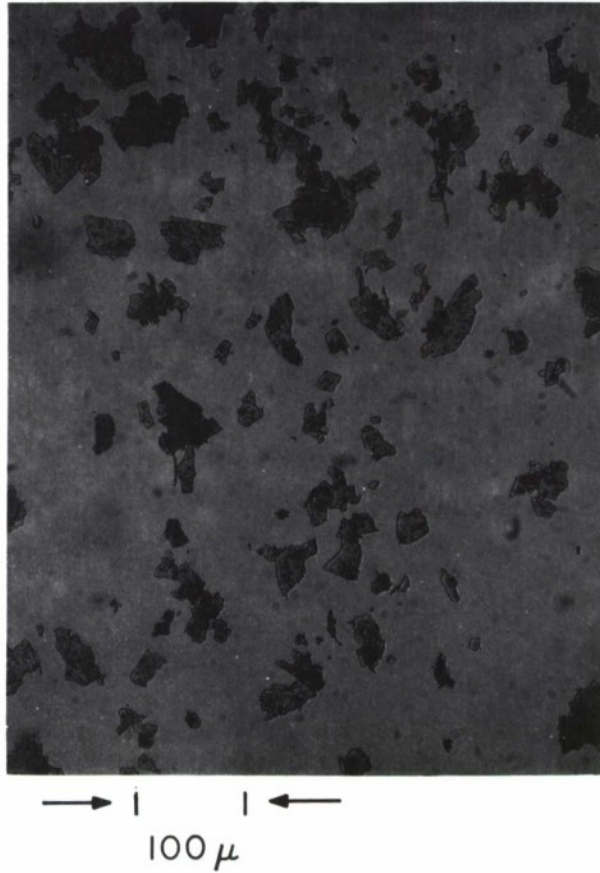Photomicrograph of SnO$_2$ Flakes

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A detailed account of a recent study in search for a material approximating the following combination of qualities:

i. A strongly "colored" reflectivity, specular or diffuse, in the near IR conforming closely to the schedule: 5u, 1.0 reflectivity; 4u, 0.9; 3u, 0.8; 2.5u, 0.7; 2u, 0.45; 1.5u, 0.3; 1.5u, 0.3; 1u, 0.2; 0.8u, 0.1.

ii. Minimum absorption at all wavelengths.

iii. Minimum weight per unit area of reflecting surface, in the order of 1 gm /meter^2 (5000 sq. ft./lb); this is the weight of a plastic foil about 1u thick.

iv. Easy dispersal, from storage in a compact form, into separated airborne flakes or bubbles, large enough (30u diameter) that differaction effects will not distort the color, yet small enough to resist deformation by ordinary air turbulence.

v. Cost, in the storage form, not exceeding $. 02/ft^2.

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